

FORM PTO-1390 (Modified)  
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

**221282US0XPCT**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

**10/089061**

INTERNATIONAL APPLICATION NO.  
**PCT/FR00/02752**

INTERNATIONAL FILING DATE  
**4 October 2000**

PRIORITY DATE CLAIMED  
**4 October 1999**

TITLE OF INVENTION

**SULFONATED POLYIMIDES, MEMBRANES PREPARED WITH THEM, AND FUEL CELL DEVICE  
COMPRISING THESE MEMBRANES**

APPLICANT(S) FOR DO/EO/US

**PINERI Michel et al.**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

**Notice of Priority/PCT/IB/308**

**Drawings (3 sheets)/PCT/IB/304**

**Cited References (1)/Form PTO-1449**

**Statement of Relevancy**

U.S. APPLICATION NO. (IF KNOWN) SEE 37 CFR  
**10/089061**INTERNATIONAL APPLICATION NO.  
**PCT/FR00/02752**ATTORNEY'S DOCKET NUMBER  
**221282US0XPCT**

24. The following fees are submitted:.

**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :**

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... **\$1040.00**
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... **\$890.00**
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... **\$740.00**
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... **\$710.00**
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... **\$100.00**

**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS PTO USE ONLY****\$890.00**Surcharge of **\$130.00** for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).☐ 20 ☐ 30**\$0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	29 - 20 =	9	x \$18.00
Independent claims	1 - 3 =	0	x \$84.00

**\$162.00****\$0.00**

Multiple Dependent Claims (check if applicable).

☐**\$0.00****TOTAL OF ABOVE CALCULATIONS =****\$1,052.00**☐ Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.**\$0.00****SUBTOTAL =****\$1,052.00**Processing fee of **\$130.00** for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).☐ 20 ☐ 30**\$0.00****TOTAL NATIONAL FEE =****\$1,052.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

☐**\$0.00****TOTAL FEES ENCLOSED =****\$1,052.00**

Amount to be:

refunded

\$

charged

\$

- a. ☒ A check in the amount of **\$1,052.00** to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

**Surinder Sachar**  
Registration No. 34,423

**22850**

SIGNATURE

Norman F. Oblon

NAME

**24,618**

REGISTRATION NUMBER

DATE

*April 4 2002*

221282US-0X PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :  
MICHEL PINERI ET AL : ATTN: APPLICATION DIVISION  
SERIAL NO: NEW U.S. PCT APPLN. :  
(Based on PCT/FR00/0275)  
FILED: HEREWITH :  
FOR: SULFONATED POLYIMIDES, :  
MEMBRANES PREPARED WITH  
THEM, AND FUEL CELL DEVICE  
COMPRISING THESE MEMBRANES

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

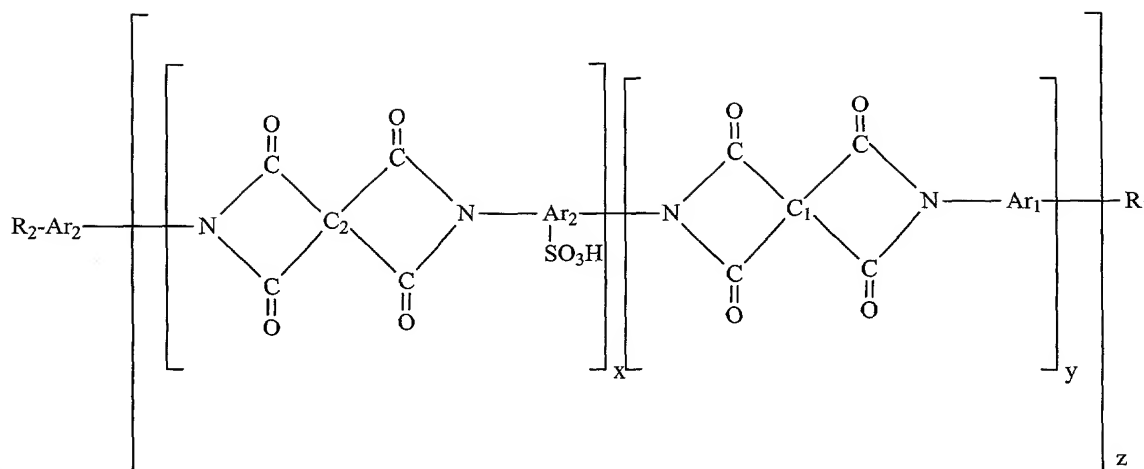
SIR:

Prior to examination on the merits, please amend the above-identified application as follows:

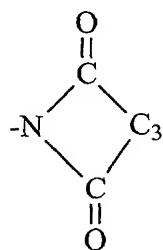
IN THE CLAIMS

Please amend the claims as shown in the marked-up copy following this amendment to read as follows.

3. (Amended) Sulfonated polyimide according to Claim 1 in which the value of x is from 5 to 9 and the value of y is from 5 to 10.
4. (Amended) Sulfonated polyimide according to Claim 1 represented by the following general formula (I):



in which C<sub>1</sub>, C<sub>2</sub>, Ar<sub>1</sub> and Ar<sub>2</sub>, x and y have the meaning given above and where each of the groups R<sub>1</sub> and R<sub>2</sub> represents NH<sub>2</sub> or a group represented by the formula:



where C<sub>3</sub> is a divalent group comprising at least one carbonaceous aromatic ring, optionally substituted, having from 6 to 10 carbon atoms and/or a heterocycle of aromatic character, optionally substituted, having from 5 to 10 atoms and comprising one or more heteroatoms selected from the group that includes S, N, and O, C<sub>3</sub> forming with the adjacent imide group a cycle with 5 or 6 atoms.

6. (Amended) Sulfonated polyimide according to Claim 1, the equivalent molecular weight defined by the polymer weight in gram per sulfonic acid equivalent of which is from 400 to 2,500.

7. (Amended) Sulfonated polyimide according to Claim 1 the molecular weight of which is from 10,000 to 100,000.

8. (Amended) Sulfonated polyimide according to Claim 1, in which in the formulas (I<sub>x</sub>), (I<sub>y</sub>), and (I), C<sub>1</sub> and C<sub>2</sub> can be identical or different, and each represents a benzenic ring optionally substituted, by one or two substituents selected from the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms; or several benzenic rings optionally substituted by one or more substituents selected from the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms, linked by a simple bond or by a divalent group between them;

- C<sub>1</sub> and C<sub>2</sub> can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms;

- C<sub>1</sub> and C<sub>2</sub> can also each represent a heterocycle or a condensated heterocycle, with aromatic character, this heterocycle being optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms;

- Ar<sub>1</sub> and Ar<sub>2</sub> can be identical or different, and each represents, for example, a divalent benzenic ring with meta or para binding, optionally substituted by one or more substituents selected from among the alkyl and alkoxy with 1 to 10 C and the halogen or several benzenic rings optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms, linked by a simple bond or by a divalent group;

- Ar<sub>1</sub> and Ar<sub>2</sub> can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms;

- Ar<sub>1</sub> and Ar<sub>2</sub> can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from among the alkyl and alcoxy groups with 1 to 10 C and the halogen atoms.

18. (Amended) Membrane comprising a sulfonated polyimide according to Claim 1.

Please add the following new claims.

20. (New) Sulfonated polyimide according to Claim 4, in which in the formulas (I<sub>x</sub>), (I<sub>y</sub>), and (I), C<sub>1</sub> and C<sub>2</sub> can be identical or different, and each represents a benzenic ring optionally substituted, by one or two substituents selected from the alkyl and alcoxy groups with 1 to 10 C and the halogen atoms; or several benzenic rings optionally substituted by one or more substituents selected from the alkyl and alcoxy groups with 1 to 10 C and the halogen atoms, linked by a simple bond or by a divalent group between them;

- C<sub>1</sub> and C<sub>2</sub> can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from the alkyl and alcoxy groups with 1 to 10 C and the halogen atoms;

- C<sub>1</sub> and C<sub>2</sub> can also each represent a heterocycle or a condensated heterocycle, with aromatic character, this heterocycle being optionally substituted by one or more substituents selected from among the alkyl and alcoxy groups with 1 to 10 C and the halogen atoms;

- Ar<sub>1</sub> and Ar<sub>2</sub> can be identical or different, and each represents, for example, a divalent benzenic ring with meta or para binding, optionally substituted by one or more substituents selected from among the alkyl and alcoxy with 1 to 10 C and the halogen or several benzenic rings optionally substituted by one or more substituents selected from among the alkyl and alcoxy groups with 1 to 10 C and the halogen atoms, linked by a simple bond or by a divalent group;

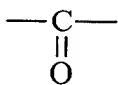
- Ar<sub>1</sub> and Ar<sub>2</sub> can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms;

- Ar<sub>1</sub> and Ar<sub>2</sub> can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms.

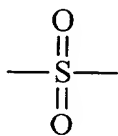
21. (New) The sulfonated polyimide according to Claim 20, in which the divalent group mentioned is selected from among:

- a divalent group derived from a linear or branched alkyl group with 1 to 10 C optionally substituted, by one or more halogens selected from among F, Cl, Br, and I and/or by one or more hydroxyl groups:

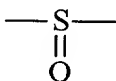
- a heteroatom selected from among O, S;



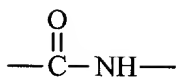
- a group ;



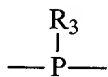
- a group ;



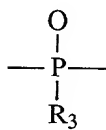
a group ;



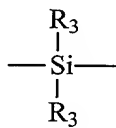
- a group ;



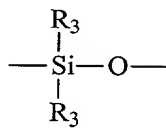
- a group ;



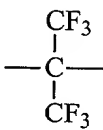
- a group ;



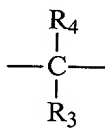
- a group ;



- a group ;



- a group ;



- a group ;



where  $R_3$  and  $R_4$  are selected from among the alkyl groups of 1 to 10 C such as methyl, ethyl, and isopropyl, etc.

22. (New) The sulfonated polyimide according to Claim 20, in which  $C_1$  is a benzenic ring, and  $C_2$  is a set of two benzenic rings linked by an oxygen bridge between them.

23. (New) The sulfonated polyimide according to Claim 20, in which  $C_1$  is comprised of benzenic cycles linked by one or more perfluororalkylene groups and  $C_2$  is comprised of benzenic rings linked by one or more divalent perfluoroalkylenes groups or perfluororalkylenes.

24. (New) The sulfonated polyimide according to Claim 20, in which  $C_1$  is a benzenic ring and  $C_2$  is a naphthalene cycle.

25. (New) The sulfonated polyimide according to Claim 20, in which  $C_1$  and  $C_2$  are both naphthalenic cycles.

26. (New) The sulfonated polyimide according to Claim 20, in which  $Ar_1$  is a diphenyl methane group, and  $C_2$  is a biphenyl disulfonic.

27. (New) The sulfonated polyimide according to Claim 20, in which  $Ar_1$  is a benzenic group and  $Ar_2$  is a biphenyl disulfonic.

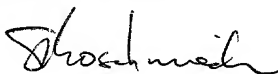
28. (New) The process according to Claim 20, in which  $Ar_1$  is a diphenyl ether group and  $Ar_2$  is a biphenyl disulfonic group.

REMARKS

Claims 1-28 are active in the present application. Claims 3, 4, 6-8 and 18 have been amended to remove multiple dependencies. Claims 20-28 are new claims. Support for the new claims is found in the original claims. An action on the merits and allowance of claims is solicited. No new matter is added.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



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**Marked-Up Copy**

Serial No:

Amendment Filed on:

4-4-02

IN THE CLAIMS

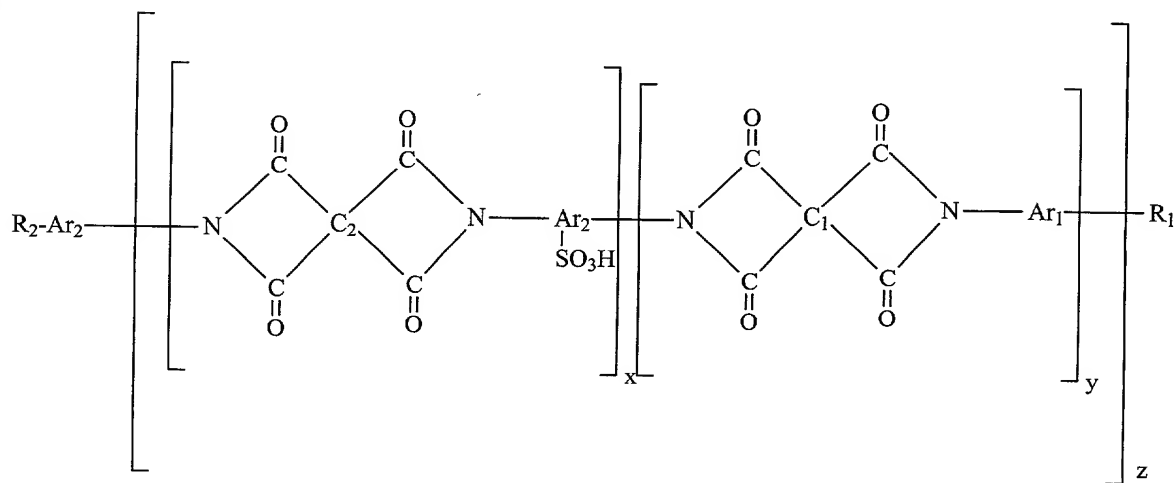
Please amend the claims as follows.

--3. (Amended) Sulfonated polyimide according to [any of Claims 1 and 2] Claim 1

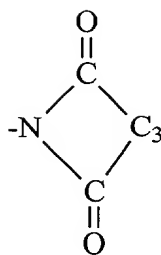
in which the value of x is from 5 to 9 and the value of y is from 5 to 10.

4. (Amended) Sulfonated polyimide according to [any of Claims 1 to 3] Claim 1

represented by the following general formula (I):



in which  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{Ar}_1$  and  $\text{Ar}_2$ ,  $x$  and  $y$  have the meaning given above and where each of the groups  $\text{R}_1$  and  $\text{R}_2$  represents  $\text{NH}_2$  or a group represented by the formula:



where  $C_3$  is a divalent group comprising at least one carbonaceous aromatic ring, optionally substituted, having from 6 to 10 carbon atoms and/or a heterocycle of aromatic character, optionally substituted, having from 5 to 10 atoms and comprising one or more heteroatoms selected from the group that includes S, N, and O,  $C_3$  forming with the adjacent imide group a cycle with 5 or 6 atoms.

6. (Amended) Sulfonated polyimide according to [any of Claims 1 to 5] Claim 1, the equivalent molecular weight defined by the polymer weight in gram per sulfonic acid equivalent of which is from 400 to 2,500.

7. (Amended) Sulfonated polyimide according to [any of Claims 1 to 6] Claim 1 the molecular weight of which is from 10,000 to 100,000.

8. (Amended) Sulfonated polyimide according to Claim 1 [or Claim 4], in which in the formulas  $(I_x)$ ,  $(I_y)$ , and  $(I)$ ,  $C_1$  and  $C_2$  can be identical or different, and each represents a benzenic ring optionally substituted, by one or two substituents selected from the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms; or several benzenic rings optionally substituted by one or more substituents selected from the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms, linked by a simple bond or by a divalent group between them;

- C<sub>1</sub> and C<sub>2</sub> can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms;

- C<sub>1</sub> and C<sub>2</sub> can also each represent a heterocycle or a condensated heterocycle, with aromatic character, this heterocycle being optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms;

- Ar<sub>1</sub> and Ar<sub>2</sub> can be identical or different, and each represents, for example, a divalent benzenic ring with meta or para binding, optionally substituted by one or more substituents selected from among the alkyl and alkoxy with 1 to 10 C and the halogen or several benzenic rings optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms, linked by a simple bond or by a divalent group;

- Ar<sub>1</sub> and Ar<sub>2</sub> can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms;

- Ar<sub>1</sub> and Ar<sub>2</sub> can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms.

18. (Amended) Membrane comprising a sulfonated polyimide according to [any of Claims 1 to 17] Claim 1.--

Claims 20-28 (New).

3/p1/

1

SULFONATED POLYIMIDES, MEMBRANES PREPARED WITH THEM,  
AND FUEL CELL DEVICE COMPRISING THESE MEMBRANES

204040-1500000  
This invention concerns sulfonated polyimides, more precisely sulfonated polyimides with an improved lifespan, which are applied to the preparation of ion-exchanging membranes, ionic conductors, notably intended for use in fuel cells, in particular low-temperature fuel cells, that is generally functioning at temperatures ranging from ambient (room) temperature up to a temperature of around 100°C.

As a result, the invention also concerns membranes prepared with the above-mentioned sulfonated polyimides with improved life span, and a fuel cell battery device, in particular of the solid electrolyte type, comprising at least one of these membranes.

The technical field of the invention may thus be defined as that of fuel cell batteries, in particular, solid electrolyte-type fuel cells.

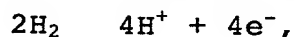
Solid polymer electrolyte-type fuel cells find their application in the electric vehicles that are currently the subject of numerous development programs, with the aim of contributing a solution to the pollution caused by vehicles with combustion engines.

Solid polymer electrolyte fuel cells could allow, by playing the role of an electrochemical energy converter, in association with an on-board energy reservoir, of, for example, hydrogen or an alcohol, to overcome these problems, notably, those of the automobile linked to the

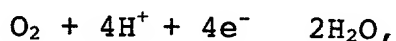
use of batteries in electric vehicles as the length of time need for recharging and of the length of time the car can be operated once charged.

The schematic assembly of a fuel cell permitting electric energy production is represented in part in Figure 1, attached hereto.

The essential component of such a cell is a ion-exchanging type of membrane formed by a polymer solid electrolyte (1), (which) serves to separate the anodic compartment (2), where there occurs oxidation of the fuel, such as hydrogen  $H_2$  (4), according to the diagram:



of the cathode compartment (3), where the oxidant, such as the oxygen in the air  $O_2$  (5) is reduced, according to the diagram:



with water production (6), while the anode and the cathode are linked by an exterior circuit (10). The water thus produced circulates between the two compartments by electro-osmosis and diffusion (arrows 11, 12).

The volumetric electrodes (13), placed on either side of the membrane, generally includes an active zone (14) and a diffusional zone (15). The active zone is composed of porous graphite covered with grains of noble metal (16), such as platinum, and a fine deposit of ion conducting polymer, with a structure similar to that of the membrane, permits the ionic transport. The diffusional zone (15) is composed of a porous rendered hydrophobic by the integration of a hydrophobic polymer

such as PTFE. The hydrophobic character permits the evacuation of the liquid water.

The protons produced on the anode, by oxidation, for example of the hydrogen on the surface of the grains of platinum, are transported (9) through the membrane to the cathode where they are combined with the ions produced by the reduction, for example, of the oxygen in the air to give water (6).

The electrons thereby produced (17) allow the fuelling of an electric engine (18), for example, placed in the exterior circuit (10), with the water as the sole by-product of the reaction.

The membrane and electrode unit is a very tiny assembly on the order of a millimetre thick, and each electrode is fuelled by the gases from behind, for example, with the aid of a corrugated plate.

The power densities obtained by this combination and which are generally on the order of  $0.5-2 \text{ W/cm}^2$  in the case in which we implement it using hydrogen and oxygen, require the combination of several of these volumetric electrode-membrane-volumetric electrode structures in order to obtain, for example, the 50kW necessary for a standard electric vehicle.

In other words, it is necessary to assemble a significant number of these structures, the elemental surfaces of which may be on the order of  $20 \times 20 \text{ cm}^2$ , in order to obtain the desired power, notably in the case where the fuel cell is implemented in an electric vehicle.



To this end, each unit formed by two electrodes and one membrane, defining a basic cell of the fuel cell, is thus set between two waterproof plates (7, 8) that provide for the distribution of the hydrogen on the anode side, on the one hand, and of the oxygen on the cathode side, on the other. These plates are called the bipolar plates.

The ion conductor membrane is generally an organic membrane containing ionic groups, which, in the presence of water, permit the conduction of the protons (9) produced on the anode by the oxidation of the hydrogen.

This membrane is several tens to several hundreds of microns in thickness and results from a compromise between the mechanical performance and the ohmic drop. This membrane also enables the separation of the gases. The chemical and electrochemical resistance of these membranes generally permits functioning off the power of the fuel cell for durations greater than 1,000 hours.

The polymer composing the membrane must thus fulfil a certain number of conditions with respect to its mechanical, physicochemical, and electric properties.

The polymer must first of all be able to produce fine films of 50 to 100 micrometers in density, without fail. The mechanical properties, breaking stress module, ductility, must make it compatible with the assembly operations including, for example, a clamping device between the metal frames.

It must be possible for the properties to be preserved as the assembly moves between states of dryness and wetness.

5 The polymer must have a good thermal stability and demonstrate good resistance to reduction and oxidation up to a temperature of  $100^{\circ}\text{C}$ . This stability is valued in terms of variation in ionic resistance and in terms of variation in mechanical properties.

10 The polymer must finally possess strong ionic conductivity. This conductivity is contributed by strong acid groups, such as phosphoric acid groups, but especially sulfonics linked to the polymer chain. Because of this, these polymers shall generally be defined by their equivalent masse, that is, by the polymer weight in 15 grams per acid equivalent.

As an example, the best systems developed today are capable of furnishing a specific power output of  $1 \text{ W.cm}^{-2}$ , or a current density of  $2 \text{ A.cm}^{-2}$  for 0.5 Volts.

20 Since 1950, numerous families of sulfonated polymers have been tested as membranes without it being possible currently to establish with certainty relations between chemical structure, morphology of the film, and performances.

25 First of all, sulfonated phenolic type resins prepared by sulfonation of polycondensated products, such as phenol-formaldehyde polymers were used.

The membranes prepared with these products were cost-effective, but do not have hydrogen stability adequate at  $50-60^{\circ}\text{C}$  for long-term applications.

Researchers then turned to derivatives of sulfonated polystyrene, which showed stability superior to that of the sulfonated phenolic resins, but cannot be used at temperatures above 50-60°C.

5       Currently, the best results are obtained with copolymers, the linear principal chain of which is perfluorinated and the side chain of which has a sulfonic acid group.

10       These copolymers are commercially available in under the DuPont Company's registered trademark NAFION® or Asahi Chemical Company's ACIPLEX-S®; others are experimental products by the DOW Company for the manufacture of the membrane designated "XUS".

15       These products have been the subjective of numerous developments and maintain their properties for several thousand hours between 80 and 100°C with current densities dependent on the partial pressures of the gases and the temperature. The current density is typically 1A.cm<sup>-2</sup> to 0.7 Volts for the Nafion® 112 with a thickness  
20       of 50 μm.

      The thermic stability of these structures, that is, in this case, the capacity to resist the acid hydrolysis and degradation by the free radicals produced during the course of the functioning of the cell, at a temperature  
25       between 60 and 100°C inclusive, for several thousand hours, has been demonstrated.

      To the criteria to be met by the membrane already indicated above should be added resistance to oxidation

contact with the oxygen of the cathodic compartment and resistance to reduction in the presence of  $H_2$ .

On the other hand, in view of the development of fuel cells that can be used for automobile power, another essential problem, now well identified by the experts, is the cost of the membrane: the latter is, along with that of the bipolar plates, the major factor affecting the production cost of the fuel cell.

In 1995, the cost of membranes produced or in development was on the order of 3,000 to 3,500 F/m<sup>2</sup>, and it is estimated that this cost must be divided by 10, even 20, to aid the industrial development of fuel cells for the automotive industry.

In order to lower these costs, poly 1.4-(diphenyl-2,6)-phenylethers sulfonated on the main chain, polyether-sulfones and polyether-ketones were synthesised and tested without really competing with the perfluorinated membranes with respect to immediate performance and durability.

In order to furnish membranes meeting the conditions already mentioned above, particularly with respect to their mechanical, physicochemical, and electrical properties, while offering a distinctly lower manufacturing cost than that prohibitive cost of manufacturing perfluorinated membranes, described above, new polymers with sulfonated polyimides were developed, which are described in the document FR-A-2 748 485. The possibility of using membranes with these sulfonated polyimides in a fuel cell was amply demonstrated by a

functioning during more than 3,000 hours with good performance.

Moreover, it has been shown that the membranes obtained with sulfonated polyimides underwent only slight degradation caused by the free radicals formed during the functioning of the cell.

In fact, during the functioning of these membranes in the fuel cell, free radicals were formed from  $H_2O_2$ , resulting from the incomplete reduction—to 2 electrons—of the oxygen and from the reaction of this hydrogen peroxide with the impurities within the membrane. The radicals OH and  $OH_2$  thus formed react with the non-perfluorinated chains, causing a break in the C-C bonds.

The break in the bonds causes in turn a loss in mechanical properties and a loss of ionic conduction by elution with short sequences containing sulfonic functions. This kind of degradation seems to occur with most non-perfluorinated polymer structures and only partial solutions allowing the elution with the sulfonic groups to be limited, for example, cross-linking, were implemented.

A simple test showing the sensitivity of the polymers to free radicals consists of immersing the membranes in an  $H_2O_2$  solution containing ferrous ions at a temperature of  $80^\circ C$ .

A similar result was indicated in the document WO-A-99/10165 for membranes obtained with polyimides containing phthalic dianhydrides.

However, if these membranes obtained from sulfonated polyimides do not suffer degradation by the free radicals formed during the functioning in the cell, they may, by contrast, be degraded by hydrolysis of the polyimides en  
5 the presence of water.

This hydrolysis reaction induces in a similar manner breaks in the chains and the elution of the sulfonic functions.

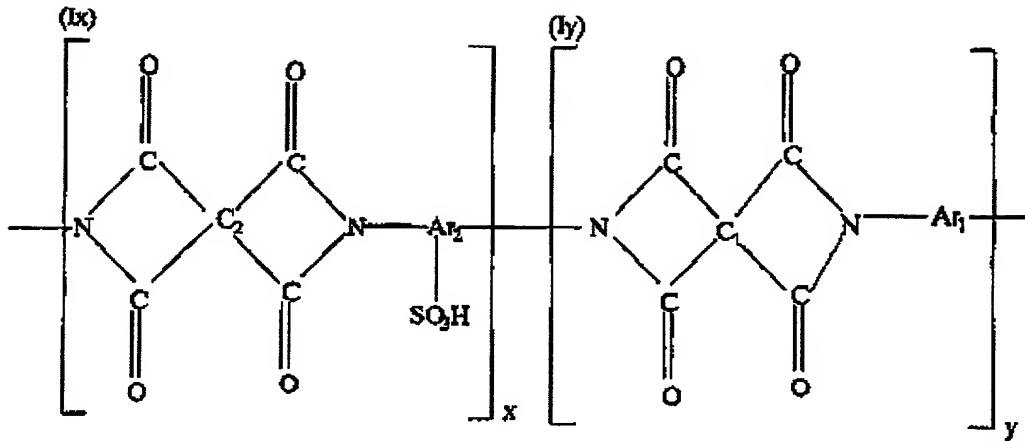
The hydrolysis thus constitutes one of the factors  
10 causing major degradation of the polyimides.

There is therefore a need for sulfonated polyimides with an improved resistance to hydrolysis.

The goal of the present invention is to provide a sulfonated polyimide polymer that meets this need.

15 The goal of the present invention is also to provide a sulfonated polyimide polymer that does not have the inconveniences, limitations, defects, and disadvantages of the sulfonated polyimides of prior art and that resolves the problems of prior art.

20 This goal and others as well have been attained, according to the invention by a block sulfonated polyimide formed by the blocks or sequences represented by the following formulas ( $I_x$ ) and ( $I_y$ ):



in which:

- x is a real number from 5 to 10; and
- y is a real number greater than or equal to x;
- 5      - and the groups  $C_1$  and  $C_2$  can be identical or different and represent each a tetravalent group containing at least one carbonaceous aromatic ring, optionally substituted, comprising 6-10 atoms of carbon and or a heterocycle of aromatic character, optionally substituted, comprising 5-10 atoms and containing one or several heteroatoms selected from S, N, and O;  $C_1$  and  $C_2$  each forming, with the adjacent imide groups, cycles of 5 or 6 atoms,
- 10      - the groups  $Ar_1$  and  $Ar_2$  can be identical or different, and each represents a divalent group comprising at least one carbonaceous aromatic ring, optionally substituted, having 6-10 carbon atoms and/or one heterocycle of aromatic character, optionally substituted, having 5-10 atoms and comprising one or
- 15      several heteroatoms selected from the group including S,
- 20

N, and O; at least one of said carbonaceous aromatic rings and/or heterocycle of  $Ar_2$  being, in addition, substituted by at least one sulfonic acid group.

Surprisingly, it has been shown that the reactions  
5 and hydrolysis that normally affect sulfonic polyimides were considerably reduced when the length of the sequence or block containing the sulfonic groups, that is, of the hydrophilic sequence or block was extended.

It turns out that the sensitivity to hydrolysis was  
10 considerably reduced for polymers of which the hydrophilic blocks or sequences were constituted by a number of repeating units (corresponding to the value of  $x$ ) from 5 to 10.

This lengthening of the hydrophilic sequence causes  
15 a similar lengthening of the hydrophobic sequence, that is, of the sequence or block that does not contain sulfonic groups.

The length of these blocks or sequences is defined  
20 by the number  $y$ , which represents the number of repeating units of hydrophobic blocks. The number  $y$  is greater than or equal to  $x$ . This number  $y$  will be, consequently, according to the invention, for example, at least equal to 5, and preferably  $y$  has a value from 5 to 40.

The polymer according to the invention made, for  
25 example, in the form of membranes, has great mechanical stability, that is, it retains all its mechanical properties, even after a prolonged period in water, in particular, no fissure is observed, even after several hundred hours at 80°C in water.

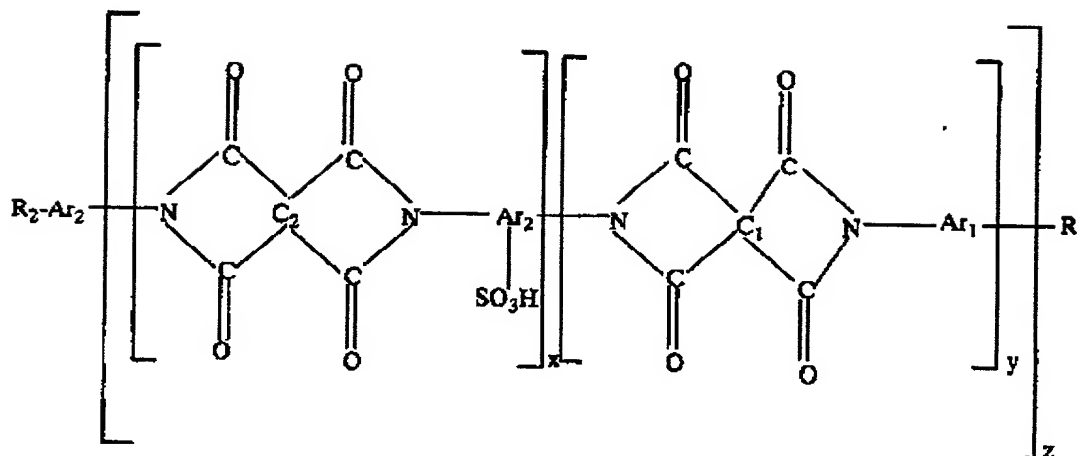


In other words, the fragilisation of the polymers according to the invention, put in the form of membranes for example, and which result from their ageing, affected by the phenomena of hydrolysis, is notably surprisingly reduced in comparison with sulfonated polyimides that do not fulfil the specific conditions with respect to the lengths of the hydrophilic blocks, defining the specific sulfonated polyimides according to the invention.

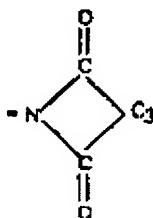
Moreover, the lengthening of the hydrophilic sequences or blocks of the polymers, according to the invention, also causes a significant diminution of the loss of mass and of the drop in conductivity, which is now observed with polymers in prior art, the hydrophilic sequences, and consequently, the hydrophobic sequences of are not as long.

Moreover, it also turns out that the resistance of the polymer according to the invention was particularly elevated for a value of  $x$  preferably from 5 to 9. This value of  $x$  corresponds to a  $y$  value from 5 to 10; the relationship  $y = x$  being verified, of course.

The copolymer of the invention may be defined as a block sulfonated copolyimide and has preferably the general following formula (I):



in which  $C_1$ ,  $C_2$ ,  $Ar_1$  and  $Ar_2$ ,  $x$  and  $y$  have the meaning given above, and where each of the groups  $R_1$  and  $R_2$  represents  $NH_2$ , or a group represented by the formula:



5

where  $C_3$  is a divalent group comprising at least one carbonaceous aromatic ring, optionally substituted, having 6-10 atoms of carbon and/or a one heterocycle with aromatic character, optionally substituted, having 5-10 atoms and comprising one or several heteroatoms selected from among S, N, and O,  $C_3$  forming with the adjacent imide group a cycle with 5 or 6 atoms.

In the formula (I) above, moreover:

-z represents a number, preferably 1 to 10, and more preferably 2 to 6.

The molecular weight of the polyimide according to the invention is generally 10,000 to 100,000, preferably from 20,000 to 80,000.

5 The equivalent molecular weight of the polyimide according to the invention is preferably 400 to 2,500, more preferably 500 to 1,200.

The equivalent molecular weight is defined by the polymer weight in grams by acid equivalent.

10 Consequently, the numbers  $z$  and  $y$  will be selected in such a manner that the equivalent molecular weight is generally 400 to 2,500, more preferably 500 to 1,200.

20 We have seen that sulfonated co polyimides are described in a general manner in the document FR-A-2 748 485. The copolymers described in this document show no  
15 resistance to hydrolysis and there is given no indication on the nature of the polymers implemented in the document, which could just as well be block or alternated, as random.

20 In that document, the length of the hydrophilic sequences or blocks and the corresponding length of the hydrophobic blocks can vary within very broad limits. It is not controlled, then, and can be selected across large ranges, from, respectively from 1 to 30 and from 1 to 20.

25 That document neither mentions nor suggests in any way, on the one hand, that the length of the hydrophilic sequences is one of the essential factors influencing the resistance to hydrolysis of the sulfonated polyimide, and, on the other hand, that this resistance to hydrolysis is improved in a surprising fashion by

selecting a length of the hydrophilic sequences superior to a specific number of repeating units or patterns and by situating oneself on a narrow range for x going from 5 to 10, and preferably from 5 to 9; this length of hydrophilic sequences influencing as a consequence the longer of the hydrophobic sequences defined by y which is found in the ranges mentioned above.

Other than the resistance to hydrolysis over a prolonged period, which is manifested by the absence of ageing and thus the maintenance of mechanical properties and of conductivity over time, the sulfonated polyimides according to the invention display all the advantageous properties of sulfonated polyimides, which are, for example, described in document FR-A-2 748 485, that is to say that the known advantageous properties of sulfonated polyimides are not affected by the fact that the sulfonated polyimides according to the invention are found to be--contrary to the sulfonated polyimide of the prior art--endowed with an excellent resistance to hydrolysis.

On the contrary, the advantageous properties are maintained over a long period of time.

Thus, the polymers according to the invention show all the properties necessary for the production of membranes and in particular of cation-exchanging membranes specifically conceived for fuel cells, and their performance is essentially compatible with an application in a fuel cell.

The invention therefore concerns a membrane comprising the sulfonated polyimide according to the invention.

5 In particular, these copolymers could easily be put in the form of films or membranes with an adequate thickness.

These polymers have a very high ion exchange capacity, greater than 0.4 meq/g, for example, from 0.8 to 2.5 meq/g.

10 The membranes comprising these polymers also have great thermic stability, notably, to acid hydrolysis at a high temperature, that is, for the most stable membranes, up to a temperature potentially as high as 100°C, for example, and can remain so, for a long period potentially  
15 as long as 3,000 hours, for example.

These conditions are the conditions of utilisation that might arise in fuel cells where the membranes described in this document have essentially been implemented.

20 Even so, the membranes comprising the polymer according to the invention have excellent resistance to reduction and to oxidation.

Finally, as described below, the polyimides according to the invention are prepared in a simple  
25 manner by means of processes tested industrially and using raw materials that are readily available and low in cost. Consequently, although the membranes obtained, as well as the fuel cells that contain these membranes show

an astonishingly increased longevity, they do not see their cost of manufacture suffer as a result.

The invention therefore concerns a fuel cell device comprising at least one membrane according to the invention.

The invention will now be described in greater detail, with reference to the attached figures, in which:

- Figure 1 is a schematic representation of a fuel cell comprising several base cells with an Electrode-Membrane-Electrode assembly, as well as bipolar plates.

- Figure 2 is a graphic that representing the change in the conductivity  $C$  in S/cm as a function of time  $t$  in hours for polymers with hydrophilic blocks of different lengths, viz., blocks of 3 repeating units (curve A); blocks of 1 unit, random polymer (curve B); 9 units block (curve C); 5 units block (curve D);

- Figure 3 is a graphic (an impedance diagram) which gives  $-I_m(Z)$  as a function of  $Re(Z)$  for a membrane made of a polymer that have hydrophilic blocks with 9 repeating units, before degradation;

- Figures 4A and 4B are impedance diagrams (NYQUIST) for membranes made of polymer that have hydrophilic blocks with 9 repeating units as a function of ageing time, i.e.,: 355 hours (curve A); 543 hours (curves B); 704 hours (curve C); 1,175 hours (curve D); 2,008 hours (curve E) and finally 2,450 hours (curve F);

- Figure 5 is a graphic that illustrates the loss of mass  $P$  in % as a function of the time of immersion in water ( $t$ ) in hours for a sulfonated polyimide the

hydrophilic sequence of which comprises 9 repeating units.

In the formulas (Ix), (Iy), and (I) cited above, C<sub>1</sub> and C<sub>2</sub> may be identical or different, and each may represent, for example, a benzenic ring optionally substituted, by one or two substituents selected from among the alkyl and alkoxy groups of 1-10 C and the halogen atoms; or several benzenic rings optionally substituted by one or several substituents selected from among the alkyl and alkoxy groups of 1-10 C and the halogen atoms, for example, of 2-4 rings, linked by a simple bond or by a divalent group.

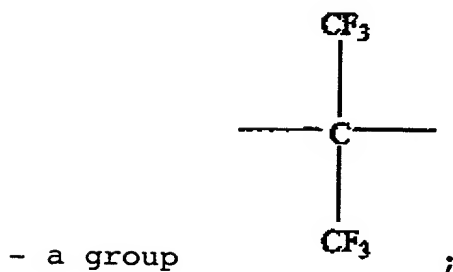
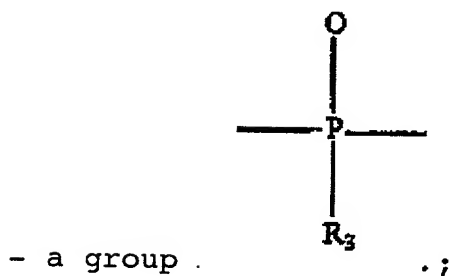
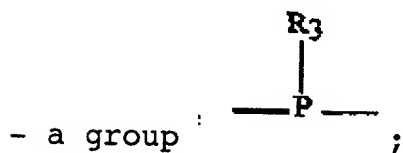
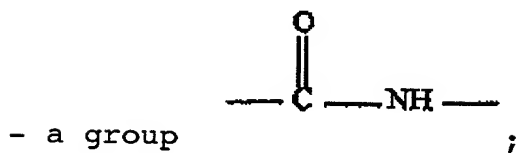
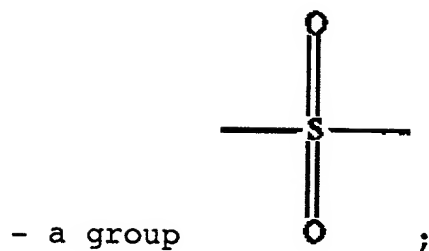
The divalent group mentioned here is selected from among, for example:

- 15 - a divalent group derived from a linear or branched alkyl group (for example, a alkylidene or alkylene group) of 1-10C optionally substituted, preferably on the same carbon, by one or more halogens selected from among F, Cl, Br, and I and/or by one or more hydroxyl groups, more
- 20 preferably the divalent group mentioned is a divalent group derived from a perfluorinated alkyl group, for example, perfluorinated alkylene.

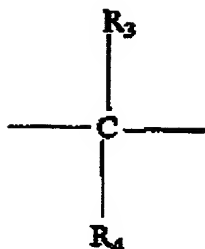
- a heteroatom selected from among O, S;



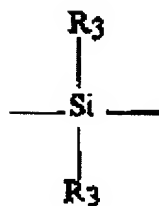
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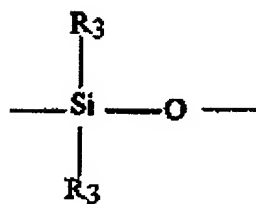


- a group ;



- a group ;

5



- a group ;

where  $\text{R}_3$  and  $\text{R}_4$  are selected from among the alkyl groups of 1 to 10 C such as methyl, ethyl, isopropyl, etc.

- 10  $\text{C}_1$  and  $\text{C}_2$  may also each represent a condensed polycyclic carbonaceous group optionally substituted by one or more substituents selected among the alkyl and alkoxy groups of 1-10C and the halogen atoms, comprising, for example, 2-5 benzenic rings selected, for example,

from among naphthalene, phenanthrene, coronene, perylene, etc.

C<sub>1</sub> and C<sub>2</sub> may also represent a heterocycle or a condensed heterocycle, aromatic in character, such as thiophene, pyridine, furan, quinoline, quinoxaline, or isobenzofuran, this heterocycle being optionally substituted by one or more substituents selected from among the 1-10 alkyl (for example, methyl, ethyl, isopropyl, etc.) and alkoxy groups and the halogen atoms (F, C, Br, I).

Among the polyimides that can be used in the framework of the invention, we shall cite those in which C<sub>1</sub> is a benzenic ring and C<sub>2</sub> a set of two benzenic rings interlinked by an oxygen bridge; or C<sub>1</sub> is constituted by benzenic rings, more preferably by two benzenic rings interlinked by one or more perfluoroalkylene groups, and C<sub>2</sub> is comprised of benzenic rings, more preferably by two benzenic rings interlinked by one or more divalent perfluoroalkyl or perfluoroalkylene groups; or C<sub>1</sub> is a benzenic ring and C<sub>2</sub> a naphthalene cycle; or C<sub>1</sub> and C<sub>2</sub> are both naphthalene cycles.

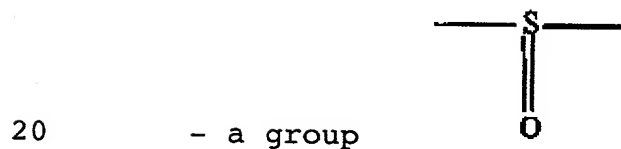
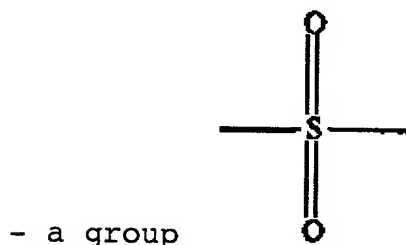
Ar<sub>1</sub> and Ar<sub>2</sub> may be identical or different, and each represents, for example, a divalent benzenic ring with meta or para chaining; optionally substituted by one or more substituents selected from among the 1-10 C alkyl and alkoxy groups such as methyl, ethyl, isopropyl, butyl, anisole, etc., and the halogen atoms; or several benzenic rings optionally substituted by one or more substituents selected from among the 1-10C alkyl and

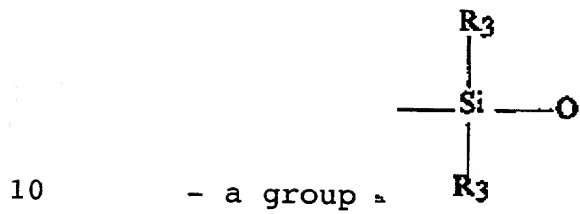
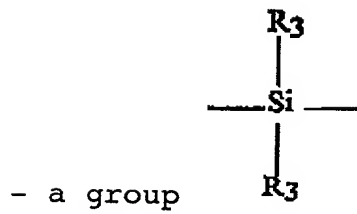
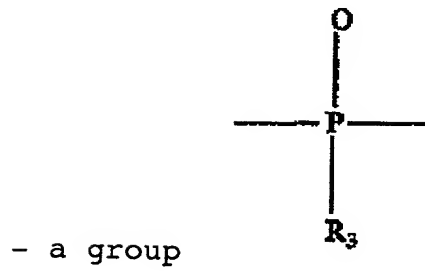
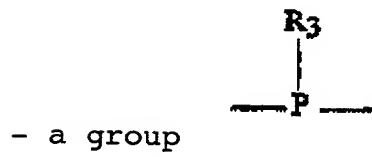
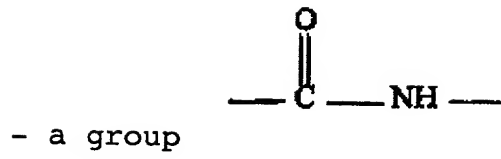
alcoxy groups and the halogen atoms, for example, with 2-5 rings, interconnected by a simple bond or by a divalent group.

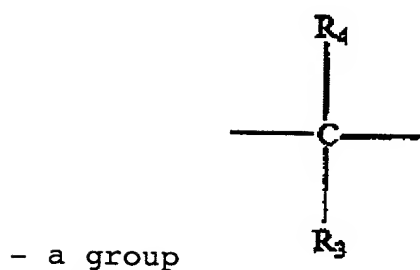
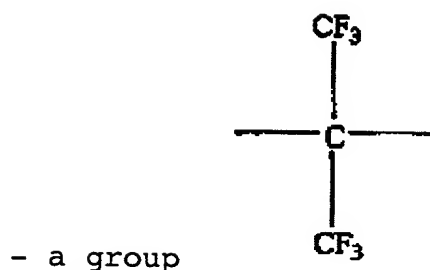
The divalent group mentioned is selected, for example, from among:

- a divalent group derived from a linear or branched alkyl (for example, an alkylidine or alkylene group) with 1-10C optionally substituted, preferably on the same carbon by one or more halogens selected from among F, Cl, Br, and I and/or by one or more hydroxyl groups; more preferably the aforementioned divalent group is a divalent group derived from a perfluorinated alkyl group, for example, perfluorinated alkylene.

- a heteroatom selected from among O, S;







where  $\text{R}_3$  and  $\text{R}_4$  are selected from among the 1-10 C  
5 alkyl groups such as methyl, ethyl, isopropyl, etc.

$\text{Ar}_1$  and  $\text{Ar}_2$  may also each represent a condensed  
polycyclic carbonaceous group optionally substituted by  
one or more substituents selected from among the 1-10 C  
alkyl and alkoxy groups and halogen atoms, selected, for  
10 example, from among naphthalene, phenanthrene, coronene,  
perylene, etc.

$\text{Ar}_1$  et  $\text{Ar}_2$  may also represent a heterocycle or a  
condensated heterocycle with aromatic character, for  
example, thiophene, pyrazine, pyridine, furan, quinoline,  
15 quinoxaline, isobenzofuran, this heterocycle being  
optionally substituted by one or more substituents  
selected from among the alkyl and 1-10 C alkoxy groups,  
for example, methyl, ethyl, isopropyl, methoxy, and the  
halogen atoms (F, Cl, Br, I).

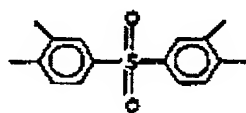
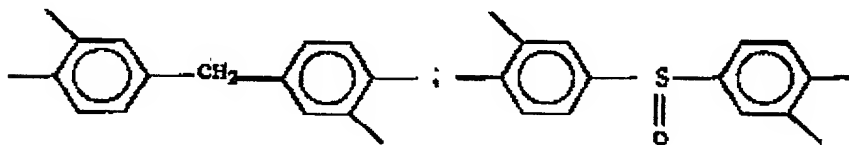
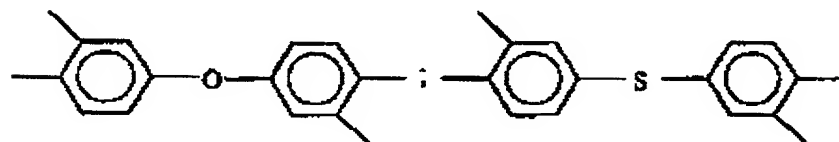
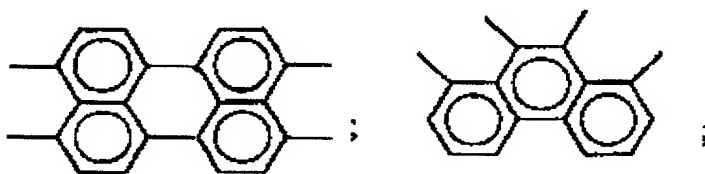
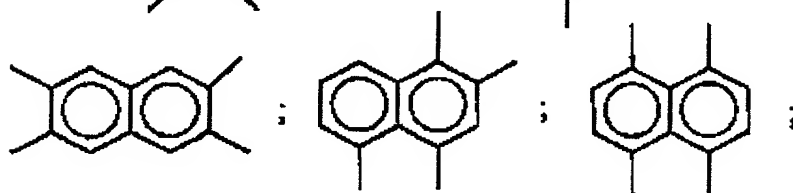
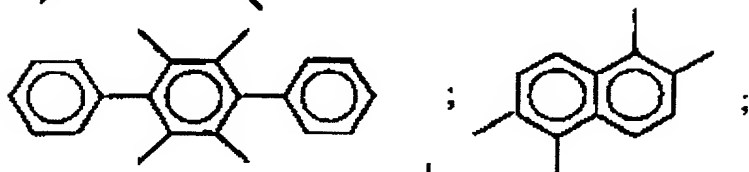
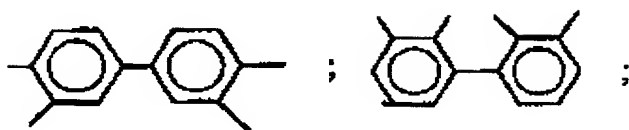
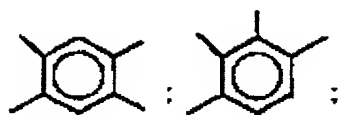
According to the invention, at least one of the cycles of  $Ar_2$ , for example, benzenic or polyphenylic or other cycle, is substituted, in addition, by one or more sulfonic acid groups.

5       The preferred polyimides are those in which  $Ar_1$  is a diphenylmethane, and  $Ar_2$  is a biphenyl-disulfonic group; or  $Ar_1$  is a benzenic group, and  $Ar_2$  a biphenyl-disulfonic group; or  $Ar_1$  is a diphenylether group, and  $Ar_2$  is a biphenyl-disulfonic group.

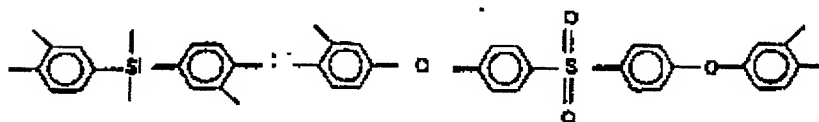
10        $C_3$  is, for example, a benzenic or naphthalene group optionally substituted by one or more substituents selected from among the 1 to 10 C alkyl and alkoxy groups and the halogen atoms.

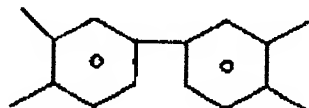
Some examples of the  $C_1$  and  $C_2$  groups are as follows:

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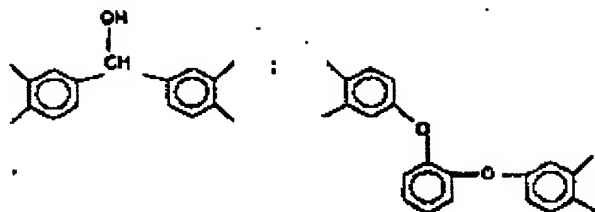


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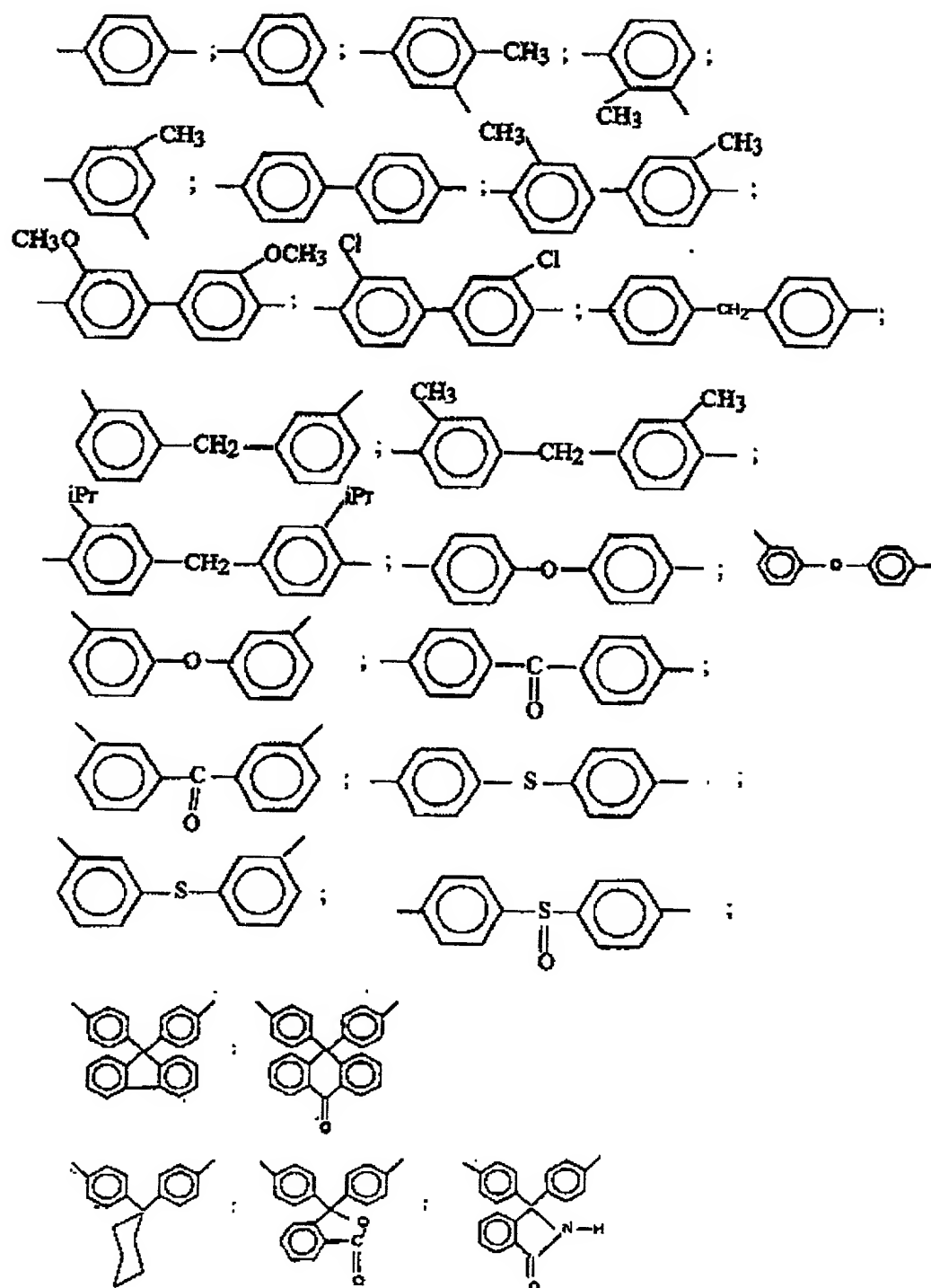


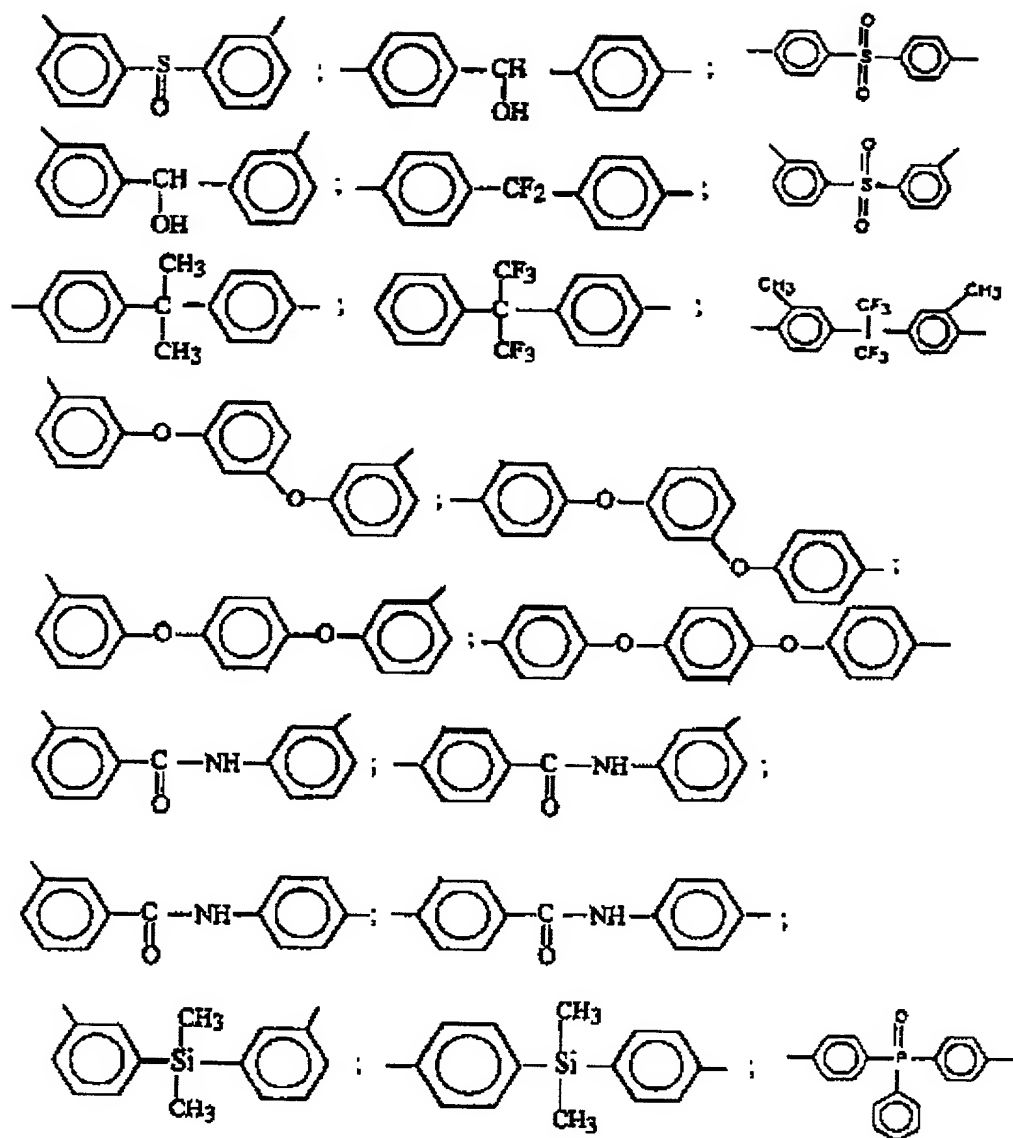


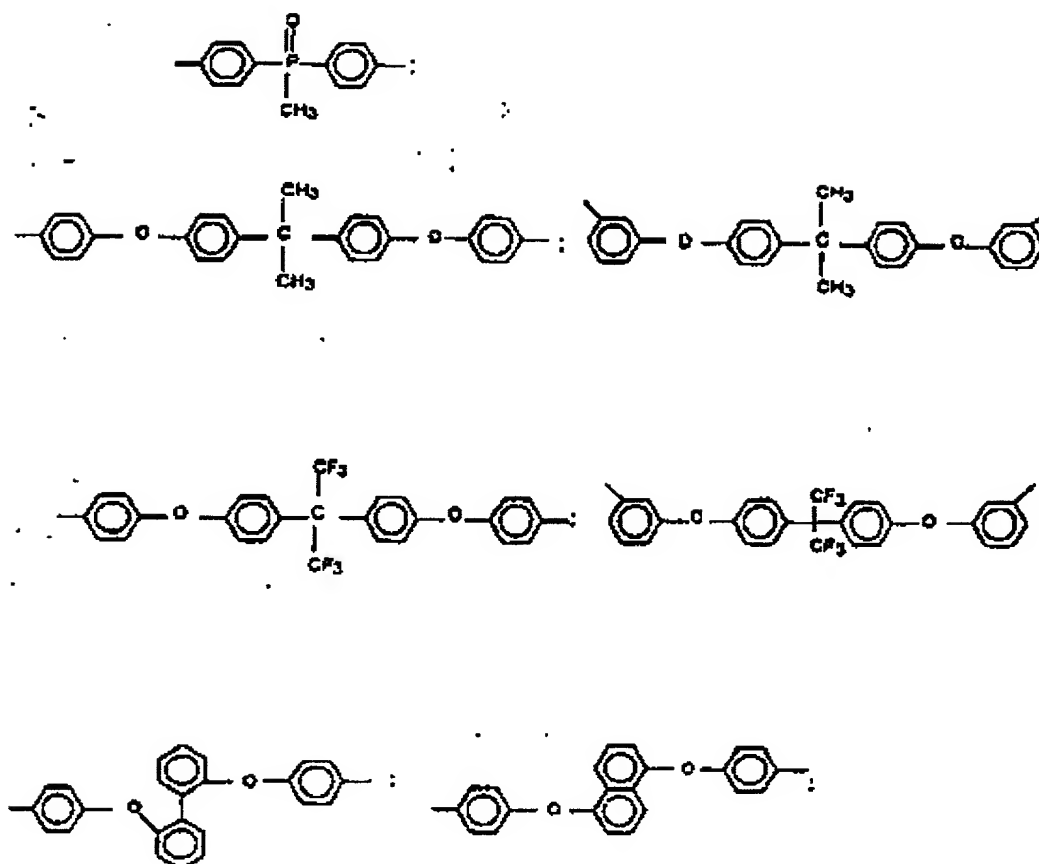




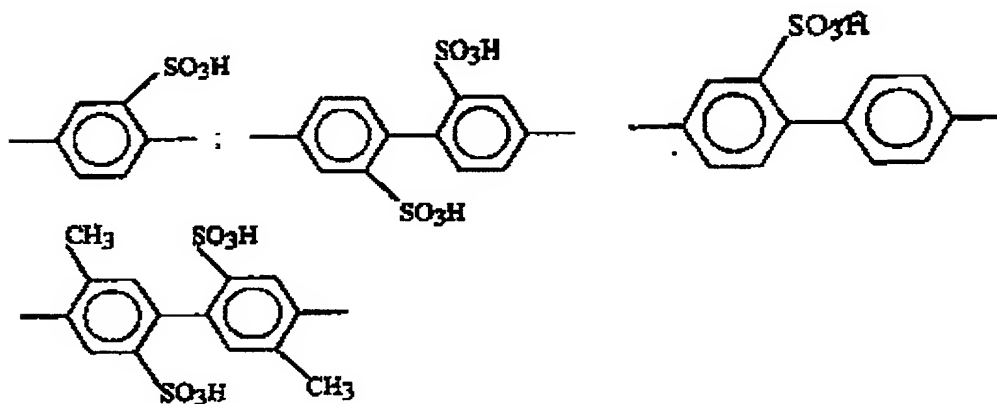
The following are some examples of the Ar<sub>1</sub> groups:





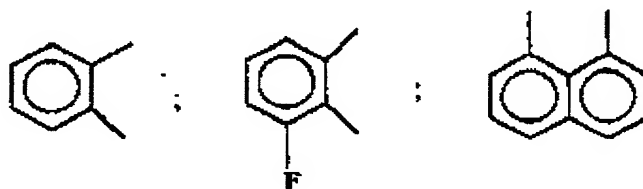


The following are some examples of the  $\text{Ar}_2$  groups:



Among the  $Ar_2$  groups, one can also cite any one of the  $Ar_1$  groups cited above having in addition one or more  $SO_3H$  groups on its ring(s) and/or heterocycles).

5 The following are some examples of the  $C_3$  groups:



10 The sulfonated polyimides according to the invention may be obtained by all processes known to those in the field to be used for the preparation of polyimides in general.

Some examples of known procedures for preparing polyimides are notably the following:

- reaction between a dianhydride and a diamine
- reaction between a Diester diacid and a diamine.

15 It is quite clear that the polyimides according to the invention can be prepared by processes that derive from the procedures cited above or by other processes that may be implemented for the synthesis of polyimides.

20 The necessary adaptations and optimisations of the procedures that are known and described in the literature may be readily made by those who work in that area.

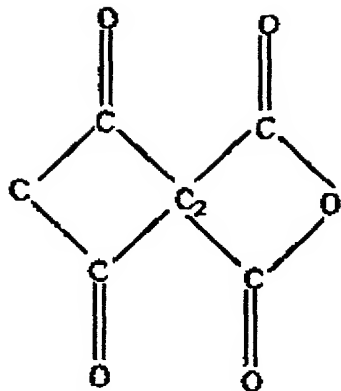
In order to prepare the polyimides according to the invention, one will preferably use the condensation of

dianhydrides on diamines through a synthesis in a two-steps process.

Such a process is commonly being implemented industrially and only requires slight adaptations to permit the preparation of the polyimides according to the invention.

The synthesis of a sulfonated polyimide according to the invention generally corresponds to the figure that follows. It is performed in two steps, generally performed in the same reactor.

In a first step, one synthesizes the hydrophilic block of sulfonated polyimide according to the invention by means of polycondensation of a dianhydride (II) with a sulfonated diamine (III).



(II)



(III)

These initial substances are products that are readily available and low in cost. Consequently, the prepared polymers, and the membranes obtained on the basis of these polymers are relative low in cost.

Among the dianhydrides represented by general formula (II) where  $C_2$  has the meaning given above, one can cite, for example, the following aromatic tetracarboxylic acid dianhydrides: benzene 1,2,3,4-tetracarboxylic acid, benzene 1,2,4,5-tetracarboxylic acid, 1,1'-biphenyl 2,3,5',6' tetracarboxylic acid, 1,1'-biphenyl 3,3',4,4'-tetracarboxylic acid, 1,1'-biphenyl 2,2',3,3'-tetracarboxylic acid, 1,1',1''-terphenyl 2',3',5',6'-tetracarboxylic acid, naphthalene 1,2,5,6-tetracarboxylic

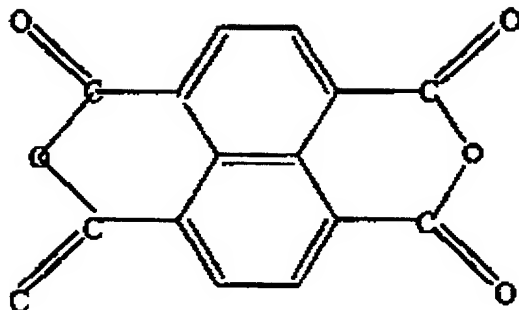
acid, naphthalene 2,3,6,7-tetracarboxylic acid,  
 naphthalene 1,2,4,5-tetracarboxylic acid, naphthalene  
 1,4,5,8-tetracarboxylic acid (DNTA), perylene 3,4,9,10  
 tetracarboxylic acid, phenanthrene 1,8,9,10  
 5 tetracarboxylic acid, 4,4'-oxybis-(benzene-1,2-  
 dicarboxylic) acid (OPDA), 4,4'-thiobis-(benzene-1,2-  
 dicarboxylic)] acid, 4,4'-sulfonylbis-(benzene-1,2-  
 dicarboxylic)] acid, 4,4'-methylenebis-(benzene-1,2-  
 dicarboxylic)] acid, 4,4'-difluoromethylenebis (benzene-  
 10 1,2-dicarboxylic) acid, 3,3'-carbonylbis-(benzene-1,2-  
 dicarboxylic) acid, 4,4'-carbonylbis-(benzene-1,2-  
 dicarboxylic) acid, 4,4'-methyl-1-ethylidene-1,1-bis  
 (benzene-1,2-dicarboxylic) acid, 4,4'-trifluoromethyl-1  
 trifluoro-2,2,2-ethylidene-1,1-bis(benzene-1,2-  
 15 dicarboxylic) acid, 4,4'-phenylene-1,3-  
 bis(carbonylbenzene-1,2-dicarboxylic) acid, 4,4'-  
 phenylene-1,4-bis (carbonylbenzene-1,2-dicarboxylic)  
 acid, 4,4'-phenylene-1,3-bis (oxybenzene-1,2-  
 dicarboxylic) acid, 4,4'-phenylene-1,4-bis (oxybenzene-  
 20 1,2-dicarboxylic) acid, 4,4'-methyl-1 ethylidene-1,1'-bis  
 (phenylene-1,4-oxy)-bis(benzene-1,2-dicarboxylic) acid,  
 pyrazine 2,3,5,6-tetracarboxylic acid, thiophene 2,3,4,5-  
 tetracarboxylic acid, and 3,3',4,4'-tetracarboxy  
 benzanilide.

25

The following are some preferred dianhydrides  
 represented by formula (II):

NTDA 1,4,5,8 naphthalene tetracarboxylic dianhydride

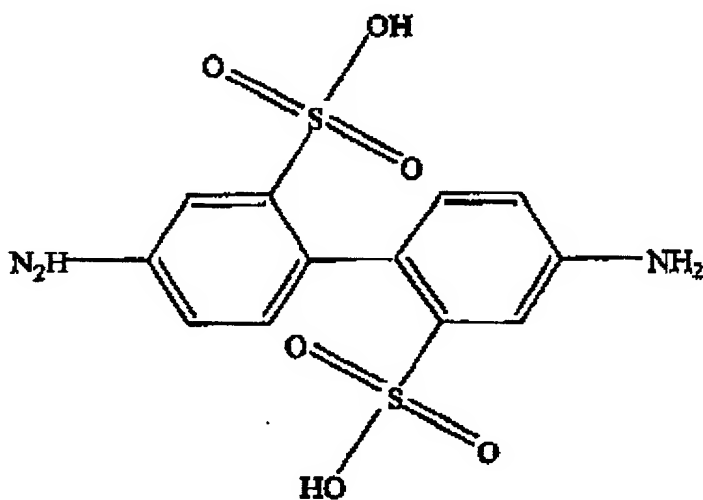




ODPA oxy-diphtalic dianhydride

- 5        Among the sulfonated diamines represented by the  
 general formula (III), where  $\text{Ar}_2$  has the meaning already  
 indicated above, one can cite as examples the following:  
 1,4 diaminobenzene 3 sulfonic acid, 4,4'-diamino biphenyl  
 2,2' disulfonic acid (BDSA), or any hydrophobic diamine  
 10 mentioned below, the  $\text{Ar}_1$  group of which is sulfonated.

One sulfonated diamine that is particularly preferred is BDSA.



Polymerization occurs at a temperature ranging from 50°C to 200°C, preferably at 180°C during a period of 2 to 48 hours, preferably 14 hours.

More precisely, in this first step, we begin by  
5 dissolving the sulfonated diamine in an appropriate solvent.

The solvent may be any solvent known to be adequate by the person experienced in that domain, as appropriate for a polycondensation reaction between a dianhydride and  
10 a diamine.

In a preferred embodiment, the solvent is a polar aprotic solvent, selected, for example, from among dimethylformamide, dimethylacetimide, and N-methylpyrrolidone, alone or in combination with, for example,  
15 aromatic solvents such as xylene or glycol ether-type solvents.

The solvent can also be a phenolic type of solvent, that is, that is selected, for example, from among phenol, 3 phenols substituted by one or more halogens  
20 (Cl, I, Br, F), the cresols (o-, m-, and p-cresol), the cresols substituted by a halogen (Cl, I, Br, F) and combinations thereof.

Preferred solvents consist in the m-cresol and a mixture of para-chlorophenol or of meta-chlorophenol and  
25 phenol, for example, in the proportions of 20% phenol and 80% para- or meta-chlorophenol.

Moreover, it is necessary, in that which can be considered a step prior to the synthesis, to transform the sulfonic acid functions of the sulfonated diamine,

such as the BDSA into a trialkylammonium salt, for example, into triethyl ammonium salt.

In fact, the sulfonated diamine is not soluble in the synthetic solvent described above, and it is therefore necessary to add to the reaction mixture a trialkylamine, for example, triethylamine, which is going to change the proton in the sulfonic group of the sulfonated diamine, by means of a trialkylammonium function and thus hinder the formation of an insoluble polysalt.

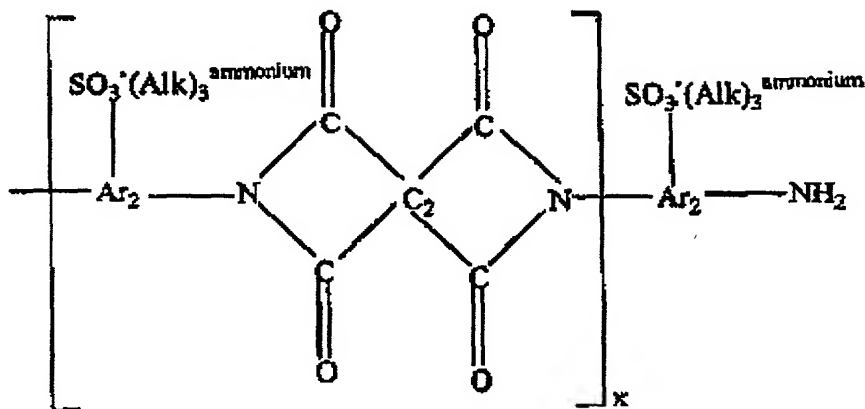
The mixture of the reagents, including trialkylamine, is effected under agitation until the sulfonated diamine is completely dissolved, and a homogeneous viscous solution has been obtained. To this solution, we then add the dianhydride(through the NTDA), as well as a catalyst: This catalyst is generally selected from among benzoic acid, etc.

Then, the mixture is heated for a first time to a temperature between 50° and 150°C, for example, at 120°C for a period of 2 to 24 hours, for example, for 12 hours, generally under mechanical agitation. Then, the polymerization, properly speaking, is achieved under the conditions described above.

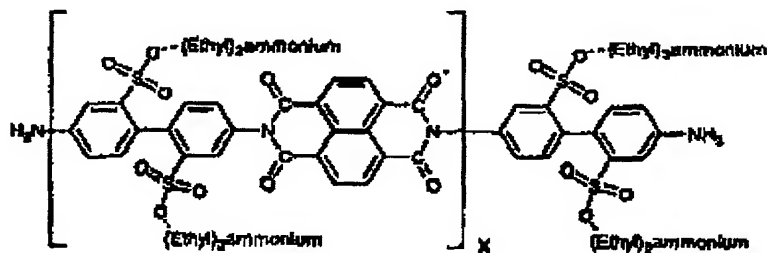
It is important that the water formed by the reaction be eliminated outside the reaction container as the reaction process occurs, by distillation, for example.

At the end of the reaction, the reactant mixture is brought back down to ambient temperature. The compound

obtained at the end of the first step is represented by the following formula:



- 5 Thus, in the case of the reaction between BDSA and and NTDA, in the presence of the triethylamine, one obtains at the end of the first step, the following compound:



- 10 In order to control the length of the ionic or hydrophilic sequence or block, one must during the course of this first step, add an excess amount of sulfonated diamine.

- 15 The molar ratio  $R_1$  of the quantities of monomers, during this first step, is defined by the following equation:

$$R_1 = \frac{n \text{ (dianhydride (II))}}{n \text{ (sulfonated diamine (III))}}$$

5        n being a number of moles and  $R_1$  being less than 1.

According to the invention,  $R_1$  should generally range from 0.33 to 0.94 in order for the length x of the hydrophilic block (which corresponds to n(sulfonated diamine)) to have the specific value according to the  
10 invention.

In a second step, we carry out the synthesis of the hydrophobic block, that is, we add to the reactant mixture obtained at the end of the first step, a certain number of moles of hydrophobic diamine (III'). The number  
15 of moles of hydrophobic diamine added is governed by the molar ratio  $R_2$  defined by the following equation:

$$R_2 = \frac{n \text{ (sulfonated diamine (III))}}{\text{(hydrophobic diamine (III))}}$$

20

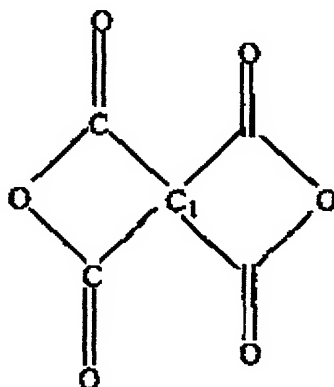
Where n (sulfonated diamine (III)) is the number of moles of sulfonated diamine (III) added during the first step.

This ratio defines the final ionic exchange capacity  
25 (CEI in meq./g.) of the polymer. In order for the value of y to be in the specific range according to the invention, the  $R_2$  ratio must generally range from 0.25 to 4, preferably from 0.42 to 1.

In order to complete the molar stoichiometry necessary for a complete reaction with the hydrophobic diamine (III') and with the sulfonated oligomer (IV) terminated by amine functions, it is necessary to add a  
 5 number of moles  $n_{\text{stoichio}}$  of dianhydride (II') according to the following solution:

$$n_{\text{stoichio}} (\text{dianhydride (II')}) = n(\text{sulfonated diamine (III)}) + n(\text{hydrophobic diamine (III')}) - n (\text{dianhydride (II)}) .$$

10 The dianhydrides represented by the general formula (II'):



where  $C_1$  has the meaning already given above, can be  
 15 selected from among the same compounds cited above, for the dianhydrides represented by formula (II).

Preferably, the anhydride represented by formula (II')

(added during the second step) is the same as the  
 20 anhydride represented by formula (II).

Among the hydrophobic diamines represented by the formula:



where  $\text{Ar}_1$  has the meaning given above, one can cite,  
 5 for example: 1,3-diaminobenzene, 1,4-diaminobenzene,  
 6-methyl-1,3-diaminobenzene, 2-methyl-1,3-diaminobenzene,  
 5-methyl-1,3-diaminobenzene, 4,4'-diamino-1,1'-biphenyl,  
 4,4'-diamino-3,3'-dimethyl-1,1'-biphenyl, 4,4'-diamino-  
 3,3'-dimethoxy-1,1'-biphenyl, 4,4'-diamino-3,3'-dichloro-  
 10 1,1'-biphenyl, methylenebis (4,4' benzene amine),  
 methylenebis (3,3'-benzene amine), methylenebis  
 (3-methyl-4,4'-benzene amine), methylenebis (3-isopropyl-  
 4,4'-benzene amine), oxybis (4,4'-benzene amine), oxybis  
 (3,3'-benzene amine), carbonylbis(4,4'-benzene amine),  
 15 carbonylis (3,3'-benzene amine), thiobis (4,4'-benzene  
 amine), thiobis (3,3'-benzene amine), sulfonybis  
 (4,4'-benzene amine), sulfonylbis (3,3'-benzene amine),  
 hydroxymethylenebis (4,4'-benzene amine),  
 hydroxymethylenebis (3,3'-benzene amine),  
 20 difluoromethylenebis (4,4'-benzene amine),  
 1-methylethylidenebis (4,4'-benzene amine), 1-  
 trifluoromethyl-2,2,2-trifluoroethylidenebis(4,4'-benzene  
 amine), 1,3-dioxyphenylenebis(3,3'-benzene amine), 1,3-  
 dioxyphenylenebis(4,4'-benzene amine), 1,4-  
 25 dioxyphenylenebis(3,3'-benzene amine), 1,4-  
 dioxyphenylenebis (4,4'-benzene amine), 3,3'-diamino-  
 benzanilide, 3,4'-diamino-benzanilide, 3',4'-diamino-  
 benzanilide, 4,4'-diamino-benzanilide, bis(3-aminophenyl)

dimethylsilane, bis(4-amino phenyl) dimethylsilane, and 9-fluoro-9-ylidene diphenylamine.

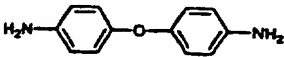
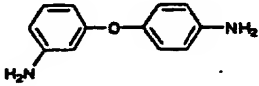
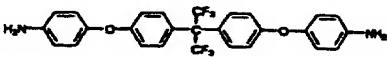
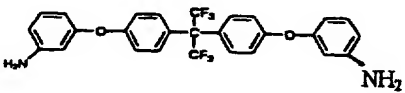
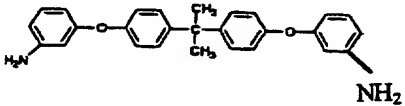
It is to be noted that one can use a mixture of several of the amines cited above in any proportions.

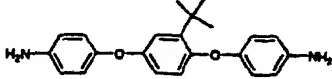
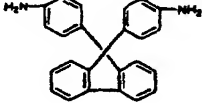
- 5 Some preferred examples of preferred hydrophobic diamines are presented in Table I (below) with the nomenclatures used and the characteristics transmitted to the final polymer by the diamines:

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Table I

Structure of the hydrophobic diamine	Nomenclature used	Characteristics
	4,4' ODA	Linear chaining (para) with the dianhydride. A single ether bridge for flexibility.
	3,4' ODA	Meta-chaining, increase of flexibility, single ether bridge
Mixture of 50% 4,4' ODA and 50% 3,4' ODA	50% 3,4' ODA	
	4,4' CF <sub>3</sub>	Linear chaining (para) with the dianhydride. Several bridges: flexible diamine
	3,3' CF <sub>3</sub>	Meta chaining and several bridges: significant flexibility
	3,3' CH <sub>3</sub>	Meta chaining and several bridges: significant flexibility

	4,4'-tButyl	Linear chaining Tertio-butyl group generating hindrance
	Cardo	Bulky diamine encouraging distancing of the chains

The added dianhydride reacts preferably with the hydrophobic diamine to form hydrophobic blocks or sequences of a length defined according to the invention.

- 5 The hydrophobic sequences or blocks react next with the ionic sequences produced during the first step in order to produce the final polymer.

The catalyst and the solvent used are generally the same as during the first step, and thermal imination  
10 generally occurs at a temperature ranging from 50°C to 200°C, for example, 180°C or 200°C during a period ranging from 2 to 48 hours, for example, for 20 or 24 hours.

More precisely, we begin by mixing the reagents,  
15 then the temperature of the solution is brought to between 15°C and 300°C, for example, to 180°C for a period of 5 to 180 minutes, for example, for a period of 90 minutes. We then add the solvent, and carry out the thermal imination, as described above.

20 At the end of the reaction, the reactant mixture is cooled to ambient temperature. The solution can then be stored in that condition or poured at a temperature of 80

to 180°C, for example, at a temperature of 160°C, into a container containing a poor polymer solvent, such as methanol or acetone, in order to precipitate the polymer.

The polymer is next filtered and washed several  
5 times, for example in boiling methanol, in order to eliminate the traces of residual solvents. It is finally dried at a temperature of 120°C, for example, preferably in a vacuum.

The regeneration of the sulfonic functions in the  
10 form of SO<sub>3</sub>H is done by immersing the polymer for a period of from 1 to 24 hours, for example, for 12 hours, at ambient temperature, in an acid solution, preferably 0.1N hydrochloric acid.

The final polymer has the following structure,  
15 defined by the formulas (Ix), (Iy), and (I) given above.

In order to differentiate the polymers studied, we can use the following nomenclature:

hydrophobic diamine nomenclature / hydrophilic block  
/ R<sub>2</sub> ratio.

20 for example:

for R<sub>1</sub> = n (dianhydride) = 4 and R<sub>2</sub> = n(sulfonated diamine) = 30  
n(sulfonated diamine) 5                      n(hydrophobic diamine) 70

The nomenclature will be 4,4' ODA 5 30/70, in the  
case where the hydrophobic diamine is ODA and where the  
25 length of the hydrophobic sequence is 5 repeating units  
(x = 5, which is in compliance with the invention).

If this same polymer comprised a hydrophobic diamine comprising 50% 3,4' ODA and 50% 4,4' ODA, we would then have the following nomenclature : 50% 3,4' ODA 30/70.

This invention also concerns a film or a membrane comprising the sulfonated polyimide described above.

The films or membranes can be prepared in a traditional manner, for example, by casting, viz., the polymer according to the invention is put into a solution with an adequate solvent, such as cresol or phenol, then poured onto a level surface such as a plate of glass, then dried to form a film that is 5 to 200  $\mu\text{m}$ . thick, for example.

The films can be used to prepare membranes, insulating, in particular, the anodic compartments of a fuel cell that is capable of functioning, for example, with the following systems:

- hydrogen, alcohols, such as methanol, at the anode;
- oxygen, air, at the cathode.

This invention also concerns a fuel cell device comprising one or more membranes comprising the sulfonated polyimide according to the invention.

Because of its excellent mechanical properties, the membrane can be subjected to the constraints (clamping, etc.) related to the assembly in such a device.

The fuel cell can, for example, correspond to the diagram already provided in Figure 1.

The invention will now be described in reference to the following examples, illustrative of the invention but not intended to limit the scope of the invention.

In the following examples, we prepare, then we study, under the same conditions (water, 80°C), the

degradation by hydrolysis of the 50% 3,4' ODA 30/70 sulfonated polyimides, the hydrophilic and hydrophobic blocks of which are of various lengths, some according to the invention, and others not.

5

#### Example 1

In this example, we describe the synthesis of the sulfonated polyimides that are used to study the degradation by hydrolysis.

10

#### 1.1 - Purification of the monomers

In order to obtain a polymer with a molecular mass that is elevated, two predominant parameters are that the monomers be pure and that the stoichiometric conditions be observed.

15

#### a - The sulfonated diamine: 4,4' Diamino Diphenyl 2,2'Disulfonic acid (BDSA)

BDSA is a commercial product sold in the form of a powder initially violet in colour, and the degree of purity of which is 70 - 80%.

20

In a 1,000 ml balloon flask, 100 g. of BDSA is added to 500 ml of water. The balloon flask is then heated for 4 hours until reflux. After cooling, the mauve solid in suspension is filtered, rinsed three times in water, and then three times in methanol, and dried in a vacuum for 12 hours at a temperature of 80°C. We obtain a white, slightly mauve, solid. The output obtained is close to

25

80%. The thermo gravimetric analysis reveals the presence of 0.6% residual water.

5 b - The Dianhydride: Naphtalene-1,4,5,8-tetracarboxylic acid dianhydride (NTDA)

The purity of the naphthalenic dianhydride NTDA is sufficient for the synthesis of the polymer. However, this product must be dried for hours in an incubator at a temperature of 140°C.

10

c - The hydrophobic diamine: ODA

The ODA utilised is a commercial product that comes in powder form, the initial degree of purity of which is 98%.

15

200 g. of ODA is introduced into a sublimator. The balloon flask is heated in a vacuum at a temperature of 200°C - 250°C. The ODA sublimes and is condensed on a cold inside surface. We break the vacuum and collect the ODA, purified and crystallized on the cold interior surface.

20

1. 2 - Synthesis of the 3,4' ODA 5 30/70 naphthalenic polyimide (length of the hydrophobic block: 5 repeating units)

25

FIRST STEP

	BDSA	NTDA	Benzoic Acid	Triethylamine
Basic formula	$C_{12}S_2O_6N_2H_{12}$	$C_{14}O_6H_4$	$C_7O_2H_6$	$C_6NH_{15}$
Molar Mass	344.36	268.18	122.12	101.19
Mass (g.)	3	1.869	1.19	2.11

During a first stage, in a 250 ml. three-necked round-botomed flask, equipped with a mechanical agitation and brushed by a light current of argon (1 bubble/second), we introduce 3 g. of BDSA (or  $8,712.10^{-3}$  mol of BDSA containing 0.6% water) and 18 g. of phenol/3-chlorophenol mixture under slow agitation. The phenol is previously heated in an incubator, because it is not liquid at ambient temperature. The slight excess of triethylamine (20% in relation to the sulfonic functions) or 2.11 g., is then added. The phenol/3-cholorophenol mixture and the triethylamine allow the dissolution of the BDSA. The triethylamine is especially going to exchange the  $H^+$  proton of the sulfonic group of the BDSA for the triethylammonium function  $(C_2H_5)_3N^+-H$ , thus preventing the formation of an insoluble polysalt. The solution then becomes homogeneous and viscous. Then 1,869 g. of NTDA (or  $6,969.10^{-3}$  ml.) is then added, as well as 1.19 g. of benzoic acid (catalyst). After a plateau of 2 hours at  $120^\circ C$  under mechanical agitation, the

temperature is raised to 180°C for 21 hours. The water generated by the reaction is eliminated gradually by distillation outside the balloon flask. In the course of the reaction, an increase in viscosity is observed. The agitation is then stopped, and we allow the reactant mixture to return to ambient temperature.

#### Second Step

	ODA	NTDA	Benzoic Acid
Basic Formula	$C_{12}ON_2H_{12}$	$C_{14}O_6H_4$	$C_7O_2H_6$
Molar Mass	200.24	268.18	122.12
Mass (g.)	2.07	5.919	3.77

In a second step, 4.07 g. of 3,4' ODA (or  $20,328 \cdot 10^{-3}$  mol), 5,919 g. of NTDA (or  $22,071 \cdot 10^{-3}$  mol) and 3.77 g. of benzoic acid are added to 41 g. of chlorophenol to obtain a solution 20% in mass. The temperature is brought to 180°C for 90 minutes. At the end of one hour, the medium is very viscous, and 50 g. of chlorophenol are added (final solution at around 12% in mass). The temperature is then brought to 200°C for 24 hours.

At the end of the reaction, the reactant mixture is cooled to ambient temperature, and the solution obtained is so viscous that it sets and no longer runs. The solution can then be stored in that condition in a flask or poured at 160°C into a container with methanol (a poor solvent) in order to precipitate the polymer. Next, the polymer is filtered, washed several times in boiling



methanol, in order to eliminate the traces of residual solvents. It is finally dried at 120°C in a vacuum for one night.

The regeneration of the sulfonic functions in  $\text{SO}_3\text{H}$  is effected by immersing the polymer for in a solution of 0.1M hydrochloric acid (0.1 N HCL) for 12 hours at ambient temperature.

1.3 - Synthesis of the 3,4' ODA 1 30/70 naphthalenic polyimide (random ; length of the hydrophilic: 1 repeating unit)

We repeat the synthesis described above in 1.2, except that the proportions of the reagents are adapted as a result.

1. 4 - Synthesis of the 3,4' ODA 3 30/70 naphthalenic polyimide (length of the hydrophilic block: 3 repeating units)

We repeat the synthesis described in 1.2, except that the proportions of the reagents are adapted as a result.

1.5 - Synthesis of the 3,4' ODA 9 30/70 naphthalenic polyimide (length of the hydrophilic block: 9 repeating units)

We repeat the synthesis described in 1.2, except that the proportions of the reagents are adapted as a result.

We prepare membranes from each of the polymers synthesized above, in the usual manner.

As the degradation appears to begin, within the first hours of immersion in water at 80°C, we follow  
5 changes in the conductivity, the swelling, and the loss of mass over the course of this period.

Each time, several samples of each membrane are studied. We also study the mechanical behaviour as a function of time for the various membranes.

10 Figure 2 shows changes in conductivity over time of immersion in water at 80°C for the various polymers studied having hydrophilic blocks of different lengths.

Table II shows the change in the increase (G(%)) and the loss of mass (M(%)) during the ageing of the  
15 membranes (B 35) with one hydrophilic sequence with 1 repeating unit (B 30) (3/2) with one 3-repeating unit hydrophilic sequence and (B29) (9/8) with one 9-repeating unit hydrophilic sequence.

Table II

Development of Swelling (G (%)) and of the loss of mass (M (M (%))), during the Ageing of 50% 3,4' ODA 30/70

5

Membranes having different Bloc Lengths

	G (%) Initial	t=23 hours	t=56 hours	t=79 hours
Random	35 36.9	G=43%, M=3% G=42.3%, M=2.4%		
3/2	39.2 36		G=47.9%, M=2.7% G=45.2%, M=2.7%	G=40.3%, M=7% G=37.2%, M=5.3%
9/8	66.2 64.2		G=109.6%, M=0.% G=110%, M=2.2%	G=97.2%, M=3% G=97%, M=3.3%

For all the samples studied, we observe an increase in the conductivity and in expansion in water, during the first hours of ageing. When the loss of mass increases, the conductivity and the swelling begin to diminish. These observations would seem to indicate a degradation by means of hydrolysis (diacid formation (increase of swelling and of conductivity), followed by elimination.

In terms of the mechanical behavior as a function of time, the static membranes are very fragile and show multiple cracks, after only 23 hours, the 3/2 membranes,

after 100 hours, the 5/4 membranes (according to the invention), after 1,000 hours, and the 9/8 membranes (in compliance with the invention), at the end of a time longer than 2,500 hours.

5        It has thus been demonstrated that sulfonated polyimides formed with long blocks (with  $x = 5$ , according to the invention) have a better mechanical stability over time, in terms of non-cracking.

### 10    Example 3

In this example, we are particularly interested in changes in the properties of the polymer with 9 repeating unit hydrophilic blocks (in compliance with the convention) that occur in the course of ageing.

15

#### 3.1 - Evolution of the mechanical properties during the Course of Ageing

20        The mechanical properties, that is, hardness  $H$  (in GPa), as a function of the indentation depth (nm); elasticity module  $E$  (in GPa), as a function of the indentation depth (nm); and the indented depth (nm), as a function of the penetration force applied (mN) were measured initially and after 2,400 hours of ageing in water at a temperature of 80°C.

25        The measurements are very irregular in that each membrane has a particularly porous structure. However, there does not seem to have been a real modification of the mechanical properties, confirming the excellent

resistance of this membrane to hydrolysis, in compliance with the invention.

### 3.2 - Changes in the conductivity

5       The conductivity was perfectly stabilised after 100 hours of ageing up to approximately 500 hours. Afterward, the conductivity declined again regularly. We shall note the appearance of a semi-circle on the impedance diagrams during the course of the ageing (Figures 4A and 4B).

10       The impedance diagram of the membrane before degradation is represented in Figure 3.

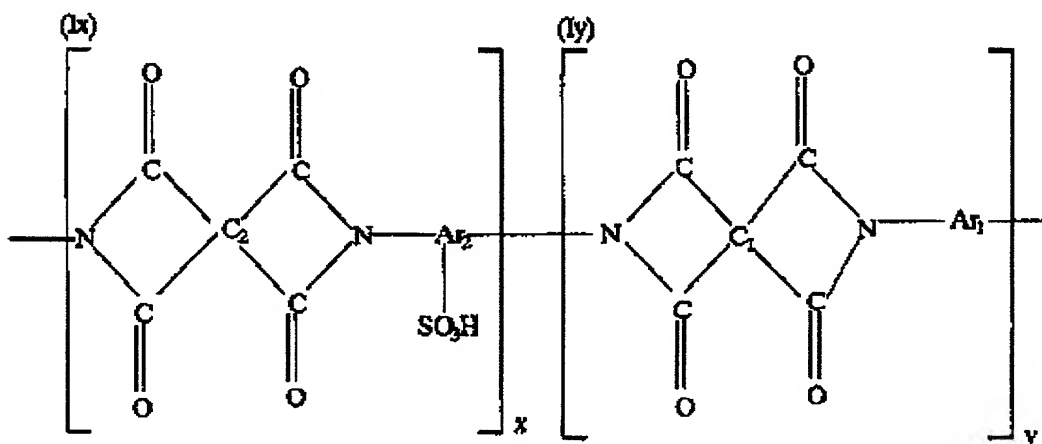
15       We observe, in Figures 4A and 4B, that the semi-circles obtained for the impedance diagrams (NYQUIST), as a function of the ageing time, are slightly off-centre. Their radius increases as a function of the length of the ageing.

### 3.3 - Loss of mass

20       The loss of mass is about 12% (Figure 5), after 2,000 hours of immersion in water at 80°C, for the polymer with long sequences (hydrophilic 9 structures). It will be recalled that, under the same conditions, the loss of mass of a 5 hydrophilic sequence polyimide is about 30%.

CLAIMS

1. Block sulfonated polyimide formed by the blocks or sequences represented by the formulas (I<sub>x</sub>) and (I<sub>y</sub>) as follows:



5

in which:

- x is a real number from 5 to 10; and
- y is a real number greater than or equal to x;
- and the groups C<sub>1</sub> and C<sub>2</sub> can be identical or different, and each represents a tetravalent group comprising at least one carbonaceous aromatic ring, optionally substituted, having from 6 to 10 carbon atoms and/or a heterocycle of aromatic character, optionally substituted, having from 5 to 10 atoms and comprising one or more heteroatoms selected from the group including S, N and O; C<sub>1</sub> and C<sub>2</sub> each forming, with the adjacent imide groups, cycles of 5 or 6 atoms,
- the groups Ar<sub>1</sub> and Ar<sub>2</sub> can be identical or different, and each represents a divalent group

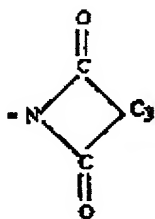
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15

20

$$\left[ \left( \text{R}_2\text{-Ar}_2 \text{---} \text{N} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{---} \text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{---} \text{N} \text{---} \text{Ar}_2 \text{---} \text{SO}_3\text{H} \right)_x \left( \text{N} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{---} \text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{---} \text{N} \text{---} \text{Ar}_1 \right)_y \text{---} \text{R}_1 \right]_z$$

in which  $C_1$ ,  $C_2$ ,  $Ar_1$  and  $Ar_2$ ,  $x$  and  $y$  have the meaning given above and where each of the groups  $R_1$  and  $R_2$  represents  $NH_2$  or a group represented by the formula:



5

where  $C_3$  is a divalent group comprising at least one carbonaceous aromatic ring, optionally substituted, having from 6 to 10 carbon atoms and/or a heterocycle of aromatic character, optionally substituted, having from 5 to 10 atoms and comprising one or more

heteroatoms selected from the group that includes S, N, and O,  $C_3$  forming with the adjacent imide group a cycle with 5 or 6 atoms.

5. Sulfonated polyimide according to Claim 4, in which in the formula (I),  $z$  represents a number from 1 to 10.

6. Sulfonated polyimide according to any of Claims 1 to 5, the equivalent molecular weight defined by the polymer weight in gram per sulfonic acid equivalent of which is from 400 to 2,500.



7. Sulfonated polyimide according to any of Claims 1 to 6 the molecular weight of which is from 10,000 to 100,000.

5        8. Sulfonated polyimide according to Claim 1 or Claim 4, in which in the formulas  $(I_x)$ ,  $(I_y)$ , and  $(I)$ ,  $C_1$  and  $C_2$  can be identical or different, and each represents a benzenic ring optionally substituted, by one or two substituents selected from the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms; or several benzenic rings optionally substituted by one or more substituents selected from the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms, linked by a simple bond or by a divalent group between them ;

10  
15        -  $C_1$  and  $C_2$  can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms ;

20        -  $C_1$  and  $C_2$  can also each represent a heterocycle or a condensated heterocycle, with aromatic character, this heterocycle being optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms ;

25        -  $Ar_1$  and  $Ar_2$  can be identical or different, and each represents, for example, a divalent benzenic ring with meta or para binding, optionally substituted by one or more substituents selected from among the alkyl and alkoxy with 1 to 10 C and the halogen or several benzenic rings optionally substituted by one or more substituents

selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms, linked by a simple bond or by a divalent group ;

5       - Ar<sub>1</sub> and Ar<sub>2</sub> can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms ;

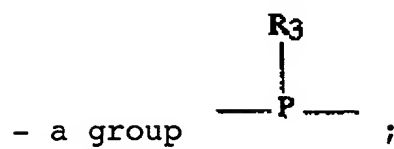
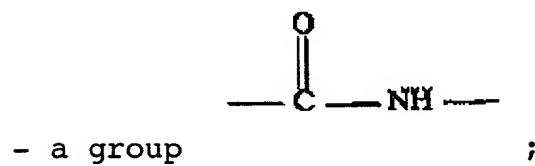
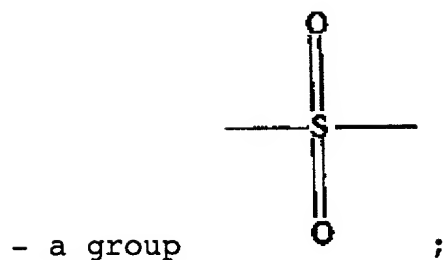
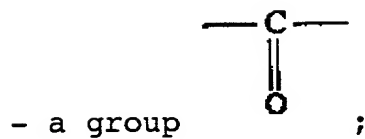
10       - Ar<sub>1</sub> and Ar<sub>2</sub> can also each represent a condensated polycyclic carbonaceous group optionally substituted by one or more substituents selected from among the alkyl and alkoxy groups with 1 to 10 C and the halogen atoms.

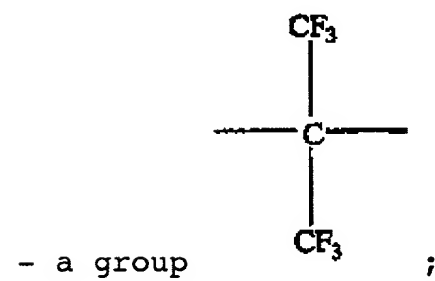
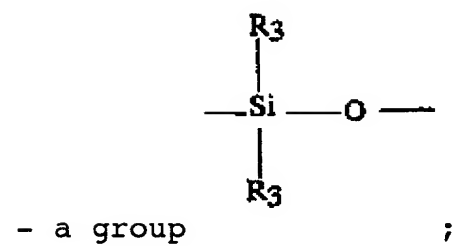
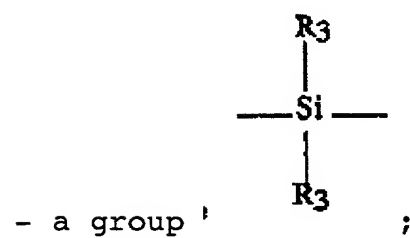
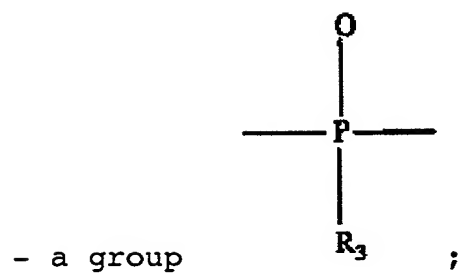
15       9. Sulfonated polyimide according to Claim 4, in which in the formula (I), C<sub>3</sub> is a benzenic or naphthalenic cycle optionally substituted by one or more substituents selected from among the 1 to 10 C alkyl and alkoxy groups and the halogen atoms.

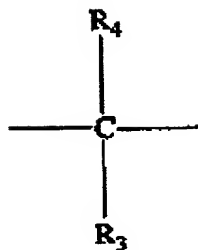
20       10. Sulfonated polyimide according to Claim 8, in which the divalent group mentioned is selected from among:

25       - a divalent group derived from a linear or branched alkyl group with 1 to 10 C optionally substituted, by one or more halogens selected from among F, Cl, Br, and I and/or by one or more hydroxyl groups:

      - a heteroatom selected from among O, S;







- a group ;

where  $R_3$  and  $R_4$  are selected from among the alkyl groups of 1 to 10 C such as methyl, ethyl, and isopropyl, etc.

11. Sulfonated polyimide according to Claim 8, in which  $C_1$  is a benzenic ring, and  $C_2$  is a set of two benzenic rings linked by an oxygen bridge between them.

12. Sulfonated polyimide according to Claim 8, in which  $C_1$  is comprised of benzenic cycles linked by one or more perfluoroalkylene groups and  $C_2$  is comprised of benzenic rings linked by one or more divalent perfluoroalkyl groups or perfluoroalkylenes.

13. Sulfonated polyimide according to Claim 8, in which  $C_1$  is a benzenic ring and  $C_2$  is a naphthalene cycle.

14. Sulfonated polyimide according to Claim 8, in which  $C_1$  and  $C_2$  are both naphthalenic cycles.

15. Sulfonated polyimide according to Claim 8, in which Ar<sub>1</sub> is a diphenyl methane group, and C<sub>2</sub> is a biphenyl disulfonic.

5        16. Sulfonated polyimide according to Claim 8, in which Ar<sub>1</sub> is a benzenic group and Ar<sub>2</sub> is a biphenyl disulfonic.

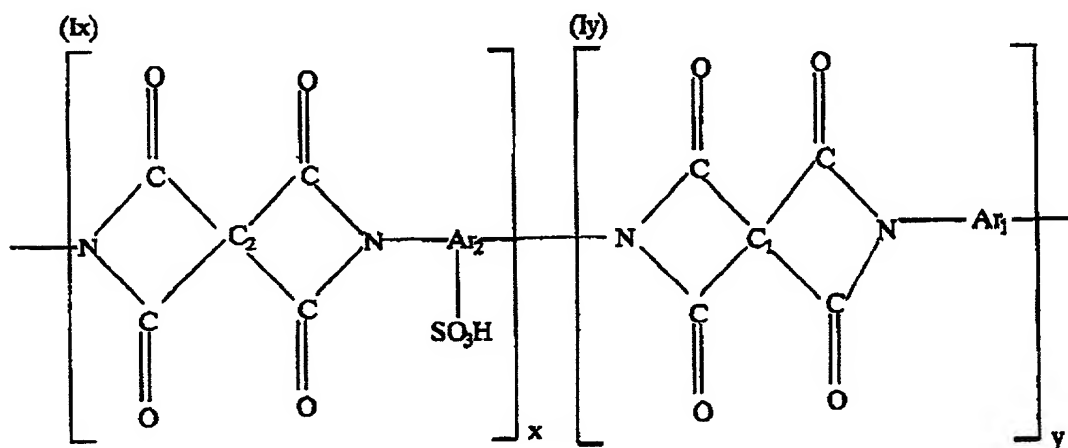
10       17. Process according to Claim 8, in which Ar<sub>1</sub> is a diphenyl ether group and Ar<sub>2</sub> is a biphenyl disulfonic group.

15       18. Membrane comprising a sulfonated polyimide according to any of Claims 1 to 17.

19. Fuel cell device comprising at least one membrane according to Claim 18.

ABSTRACTSULFONATED POLYIMIDES, MEMBRANES PREPARED WITH THEM, AND  
FUEL CELL DEVICE COMPRISING THESE MEMBRANES

Block sulfonated polyimide formed by the blocks or sequences represented by the following formulas (Ix) and (Iy):



5 in which:

- x is a real number from 5 to 10; and
  - y is a real number greater than or equal to x;
  - and the groups C1 and C2 can be identical or different, and each represents a tetravalent group
- 10 comprising at least one carbonaceous aromatic ring , optionally substituted, having from 6 to 10 carbon atoms and/or a heterocycle of aromatic character, optionally substituted, having 5 to 10 atoms and

comprising one or more heteroatoms selected from the group including S, N et O; C1 and C2 each forming, with the

adjacent imide groups, cycles of 5 or 6 atoms,

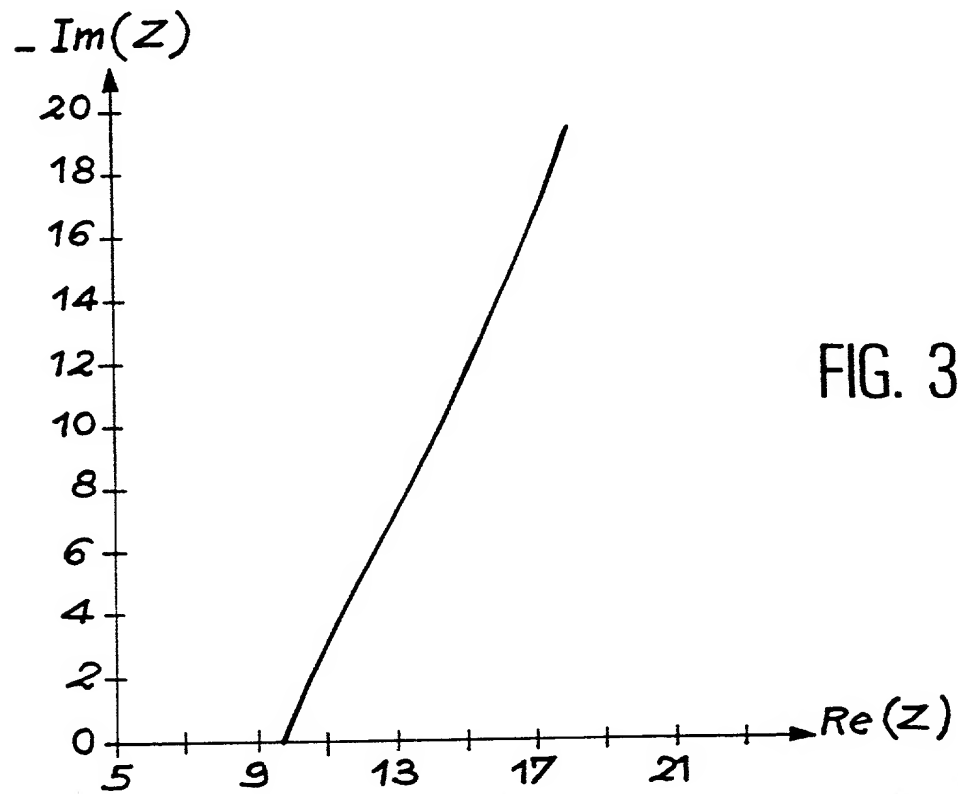
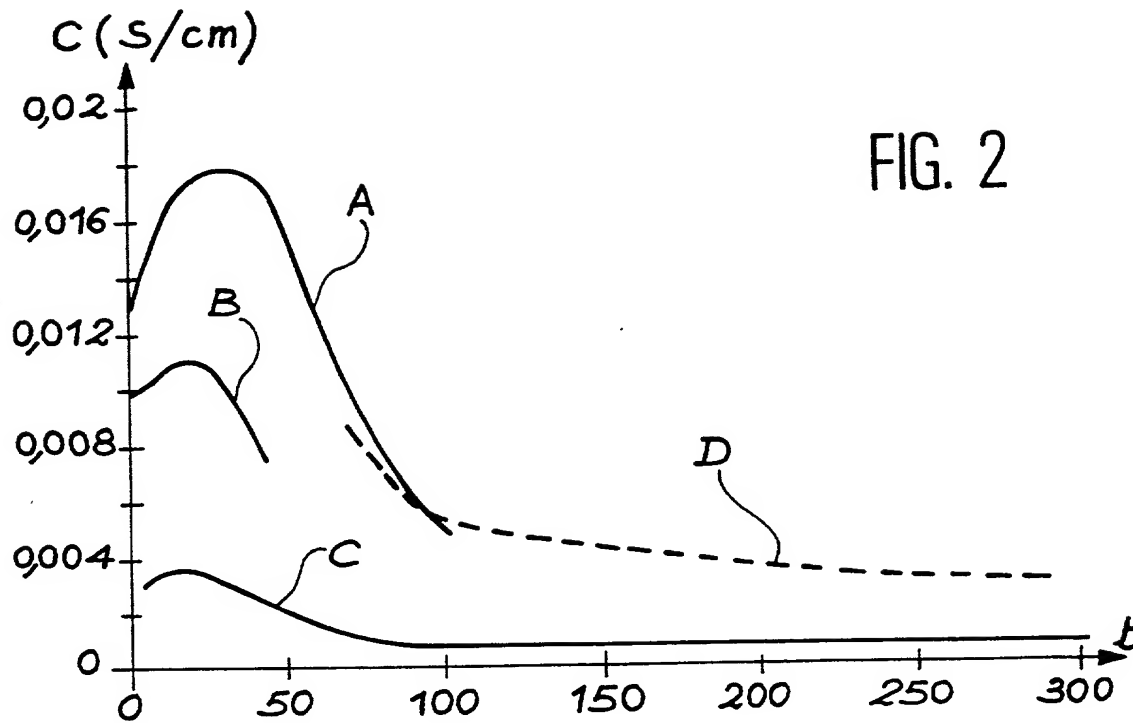
- 5        - the groups  $Ar_1$  and  $Ar_2$  can be identical or different, and each represents a divalent group comprising at least one carbonaceous aromatic ring, optionally substituted, having from 6 to 10 carbon atoms and/or a heterocycle aromatic in character, optionally
- 10 substituted, having from 5 to 10 atoms and comprising one or several heteroatoms selected from the group including S, N, and O; at least one of the carbonaceous aromatic rings and/or  $Ar_2$  heterocycle being, moreover, substituted by at least one sulfonic acid group.
- 15        Membrane comprising the sulfonated polyimide and fuel cell device comprising at least one of these membranes.

No figure

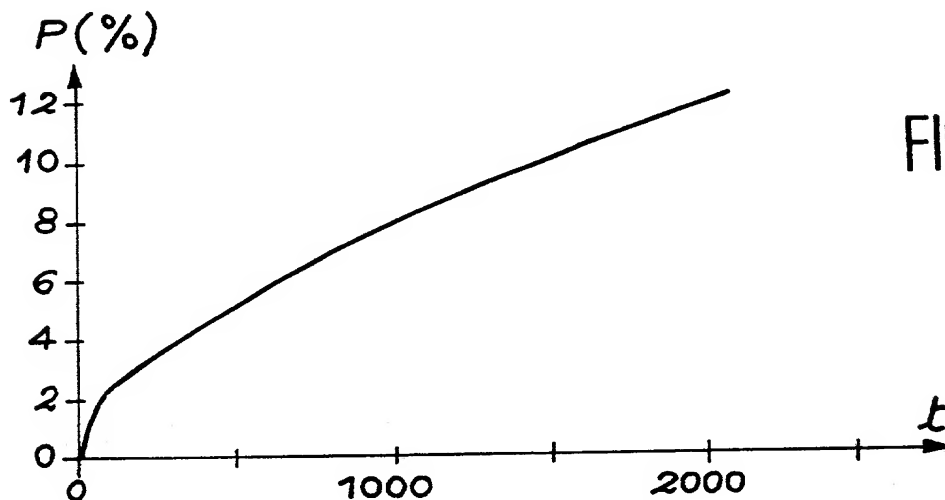
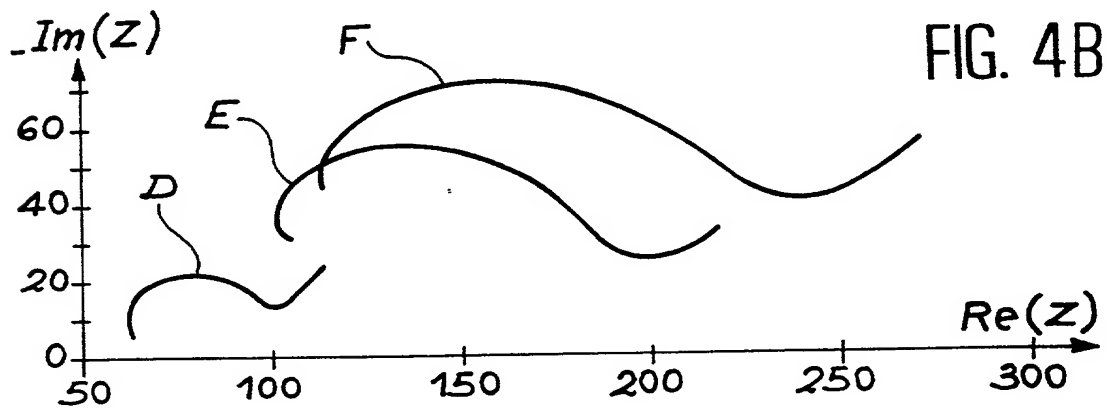
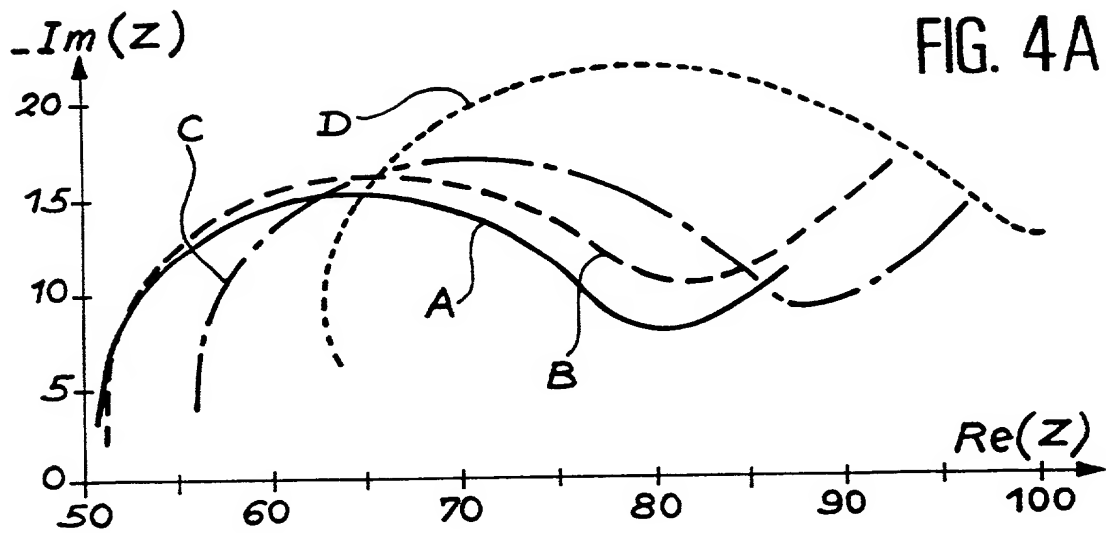


FIG. 1

2/3



3/3



*Declaration, Power Of Attorney and Petition*

Page 1 of 3

WE (I) the undersigned inventor(s), hereby declare(s) that :

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

SULFONATED POLYIMIDES, MEMBRANES PREPARED WITH THEM, AND FUEL CELL DEVICE COMPRISING THESE MEMBRANES

the specification of which

☐ is attached hereto.

☐ was filed on

as Application Serial No.

and amended on

☒ was filed as PCT international application

Number PCT/FR00/02752

on October 04, 2000

and was amended under PCT Article 19

on

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) or § 365 (b) of any foreign application(s) for patent or inventor's certificate, or § 365 (a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application (s)

Application No.	Country	Day/month/Year	Priority Claimed	
99 12356	FRANCE	04 OCTOBER 1999	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
_____	_____	_____	<input type="checkbox"/> YES	<input type="checkbox"/> NO
_____	_____	_____	<input type="checkbox"/> YES	<input type="checkbox"/> NO
_____	_____	_____	<input type="checkbox"/> YES	<input type="checkbox"/> NO

We (I) hereby claim the benefit under Title 35, United States Code, § 119 (e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. §120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

Status (pending, patented,  
abandoned)

And we (I) hereby appoint : Norman F. Oblon, Registration Number 24,618; Marvin J. Spivak, Registration Number 24,913; C. Irvin McClelland, Registration Number 21,124; Gregory J. Maièr, Registration Number 25,599; Arthur I. Neustadt, Registration Number 24,854; Richard D. Kelly, Registration Number 27,757; James D. Hamilton, Registration Number 28,421; Eckhard H. Kuesters, Registration Number 28,870; Robert T. Pous, Registration Number 29,099; Charles I. Gholz, Registration Number 26,395; William E. Beaumont, Registration Number 30,996; Jean-Paul Lavalleye, Registration Number 31,451; Stephen G. Baxter, Registration Number 32,884; Richard L. Treanor, Registration Number 36,379; Steven P. Weihrouch, Registration Number 32,829; John T. Goolkasian, Registration Number 26,142; Richard L. Chinn, Registration Number 34,305; Steven E. Lipman, Registration Number 30,011; Carl E. Schlier, Registration Number 34,426; James J. Kulbaski, Registration Number 34,648; Richard A. Neifeld, Registration Number 35,299; J. Derek Mason, Registration Number 35,270; Surinder Sachar, Registration Number 34,423; Christina M. Gadiano, Registration Number 37,628; Jeffrey B. McIntyre, Registration Number 36,867; William T. Enos, Registration Number 33,128; Michael E. McKabe Jr., Registration Number 37,182; Bradley D. Lytle, Registration Number 40,073 and Michael R. Casey Registration Number 40,294; our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P.C., whose post Office Address is : Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true ; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardise the validity of the application or any patent issuing thereon.

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Signature of Inventor

March 20, 2002  
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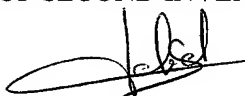
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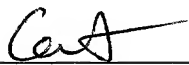
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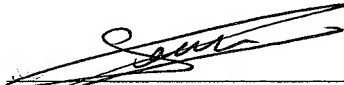
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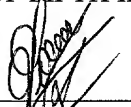
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